

# **Transient Step Permeametry on Borehole Cement and the Effect of Water**

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# Transient Step Permeametry on Borehole Cement and the Effect of Water

## Abstract

Recently the underground storage of CO<sub>2</sub> has been suggested as an interesting concept for reducing the concentration of CO<sub>2</sub> in the atmosphere. This research is focused on this method and investigates the permeability of cement used to seal the boreholes through which CO<sub>2</sub> is injected underground. In addition, the effect of water on the permeability of cement has been tested. A transient step permeametry method is used to measure the permeabilities, and both CO<sub>2</sub> and argon are used as permeametry fluids. The results for dry cement were as expected and comparable to results of earlier studies, with permeabilities in the order of 10<sup>-16</sup> to 10<sup>-17</sup> m<sup>2</sup>. Wet cement turned out to have significantly lower permeabilities caused by the presence of water. Three hypotheses were developed to explain the effect of water. It was concluded that two of them, precipitation of calcite and a lowered permeability as a result of capillary pressure, possibly take place, or a combination of these two processes. Furthermore there are indications that the Klinkenberg effect occurs in the samples. Calculations show the Klinkenberg permeability is lower than the permeabilities resulted from experiments, which was as expected. But this Klinkenberg permeability could only be determined for one sample and because of that it is not a very reliable conclusion.

## 1. Introduction

It has become widely accepted that the emission of carbon dioxide (CO<sub>2</sub>) contributes to global warming. A large amount of research has been done to develop methods to decrease the amount of CO<sub>2</sub> emission into the atmosphere. Sequestration of CO<sub>2</sub> in for example deep (saline) aquifers, unmineable coal seams and abandoned hydrocarbon reservoirs has become a serious option to accomplish this (e.g. Bachu, 2000; Holloway, 2001). To store CO<sub>2</sub> in these formations either new boreholes have to be drilled or old wells in abandoned fields can be used for the injection. After the process of injection is completed these boreholes have to be sealed, usually ENCI Portland cement Class A is used. This type of cement is known to be highly porous, with about 40% porosity, which potentially also indicates a relatively high permeability, if the connectivity is sufficient. In that case these boreholes will become weak areas in the caprock that are sensitive for CO<sub>2</sub> leakage, allowing stored gas to migrate towards these boreholes and escape to the surface. It is important to have accurate information about the permeability of this cement to CO<sub>2</sub> before storing large amounts of gas underground. A high permeability can cause serious leakage problems resulting in environmental damage, health risks etc (Bruant et al., 2002). If the amount of leakage becomes significant the use of this type of cement as a seal for boreholes needs to be reconsidered and other possible solutions have to be developed.

Extensive research has already been done about the influence of CO<sub>2</sub> on the integrity of well bore cement and potential leakage from storage formations (e.g. Gasda et al., 2004; Scherer et al., 2005; Carey et al., 2007; Liteanu et al., 2009). Leakage can occur by both mechanical and chemical effects.

Mechanical failure causes the formation of faults and fractures in the caprock or well bore plugs, which has a high potential for leakage (e.g. Bonett & Pafitis, 1996; Mainguy et al., 2007; Liteanu et al., 2009). Furthermore, the chemical effect of CO<sub>2</sub> on the porosity and permeability of wellbore cement by interactions and chemical alteration has been investigated (e.g. Onan, 1984; Duguid et al., 2006; Kutchko et al. 2006; Carey et al., 2007; Brandvoll et al., 2009; Strazisar et al., 2009; Wigand et al., 2009). Carey et al. (2007) showed that carbonation reactions decrease the porosity and permeability of wellbore cement and improve the sealing capacity. For this research cement samples were used from a wellbore in a caprock horizon within the SACROC Unit, in the Permian Basin of West Texas. This wellbore has been exposed to supercritical CO<sub>2</sub> and was altered for about 30 years.

To investigate the permeability of ENCI Portland cement Class A transient step permeametry tests were performed, using different background pressures. The temperature and pressure difference was kept constant. In addition to cement also the permeability of an anhydrite sample was measured and attempts have been done to measure the permeability of a few bituminous coal samples. For the calculation of the permeabilities a modification of the permeametry model of Sutherland and Cave (1980) was used. Furthermore, the effect of the presence of water on the permeability of this cement was studied. It was expected water has a permeability lowering effect because it decreases the connectivity between the pores. Two hypotheses have been developed to explain how water can have a decreasing effect on the permeability; by a chemical reaction or by a capillary pressure effect. And one hypothesis explains the low permeabilities by an error in the equation of state.

Also the possible presence of the Klinkenberg effect (Klinkenberg, 1941), which alters the permeability to gas of a material depending on the pore sizes, is taken into account and investigated. The Klinkenberg effect states that the permeability to a gas is a function of the mean free path of the gas molecules, and therefore depends on several parameters that determine the mean free path like pressure and temperature. Highly permeable materials are generally not affected by this effect because the pores are large enough. Yet, low permeability materials are often influenced by the Klinkenberg effect because of their small pore sizes and poor connectivity. The Klinkenberg effect is based on the occurrence of slip along pore walls. Kundt and Warburg (1875) showed that when a gas is flowing along a solid wall, the layer of gas next to the wall has a finite velocity with respect to the wall, resulting in a larger permeability than would be expected from Poiseuille's law. When the amount of slip decreases with decreasing pressure, the permeability increases. Using this theory Klinkenberg has derived a formula to calculate the "apparent" permeability of a material to a gas. The graph of this formula plots the permeability against the reciprocal mean pressure. Extrapolating this graph to infinite pressure, which is equal to the liquid permeability, gives the "true" permeability.

The goal of this study is to determine the permeability of borehole cement and the effect of water on the permeability. Test results will give permeability values and how they change with background pressure. The addition of water to the samples will make it possible to compare the results of dry and wet cement to determine the effect of water on the connectivity. If the results show that permeabilities are significantly high the use of this type of cement needs to be reconsidered. Or maybe a slight change in the procedure can be enough to overcome leakage problems. Even if the permeability of cement itself is not low enough, but the effect of water lowers the permeability enough to make transport rates acceptable this can be a solution for the problem.

## 2. Methods

In order to determine the CO<sub>2</sub> permeability of cement that is commonly used to seal boreholes after CO<sub>2</sub> injection, transient step permeametry tests were performed on this type of cement, using different background CO<sub>2</sub> and argon pressures. Furthermore the effect of water is taken into account. This section describes the methods used to execute these tests. The type of apparatus will be described and furthermore the process of sample preparation, experimental procedures, downstream volume calibration, data processing, and the used permeametry model will be explained. The results obtained by these experiments will give permeability values, which can be used to determine the amount of leakage and give an indication of the possible risks involved with the underground storage of CO<sub>2</sub>.

### 2.1 Apparatus

The apparatus used for this research (schematic overview in fig. 2.1) creates a flow through the samples by applying a transient step in pressure. The entire apparatus is submersed in a silicon oil bath, set to keep the temperature controlled at about 45°C (± 0.1°C). Furthermore, the system contains metal-metal seals instead of polymer o-rings because supercritical CO<sub>2</sub> reacts with, and is transported through the polymer.

The measurement part of the apparatus is divided in an upstream side and a downstream side. Each part is connected to a pressure transducer. It turned out to be very difficult to keep a constant upstream pressure during the experiments. For that reason a modification of the permeametry model of Sutherland & Cave (1980), which takes into account a change in upstream pressure, was used. The

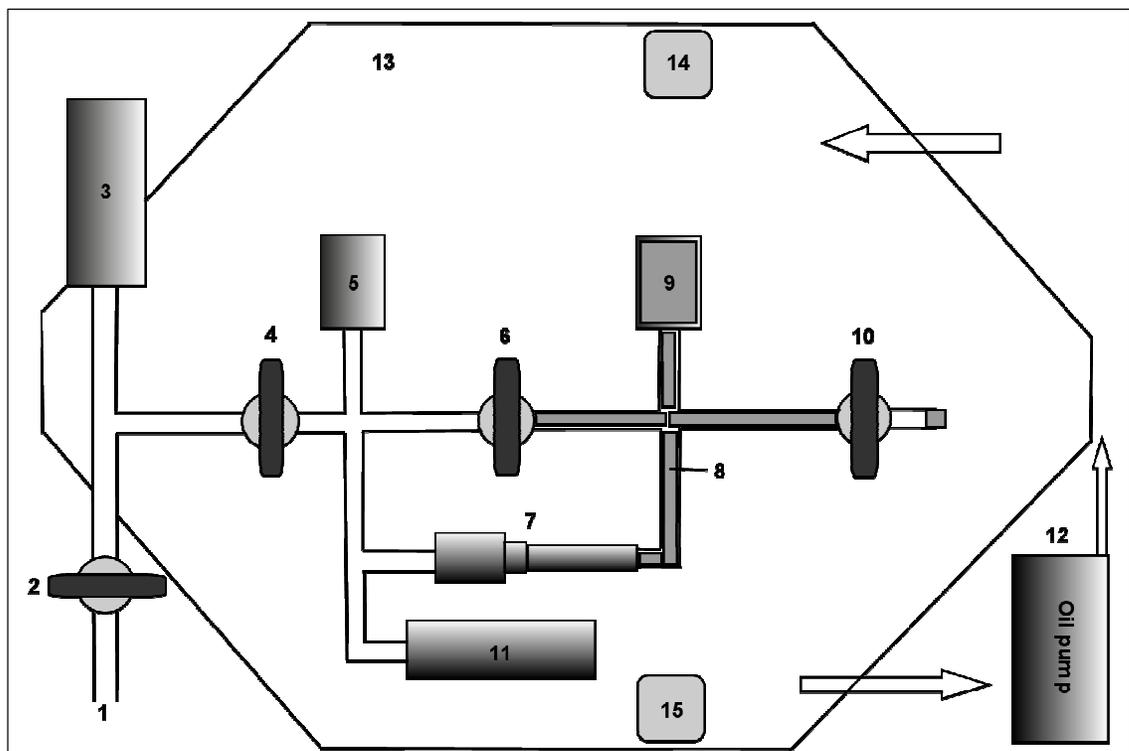


Fig. 2.1: Schematic overview of apparatus set up. 1: Fluid inlet; 2,4,6,10: Valves; 3: Conventional pressure transducer; 5: Upstream pressure transducer; 7: Sample holder; 8: Steel fillers reducing downstream volume; 9: Downstream pressure transducer, contains steel filler; 11: Additional volume at upstream side; 12: Oil pump; 13: Octagonal shaped oil bath for better circulation of oil; 14,15: Heaters, keep a controlled temperature of 45°C.

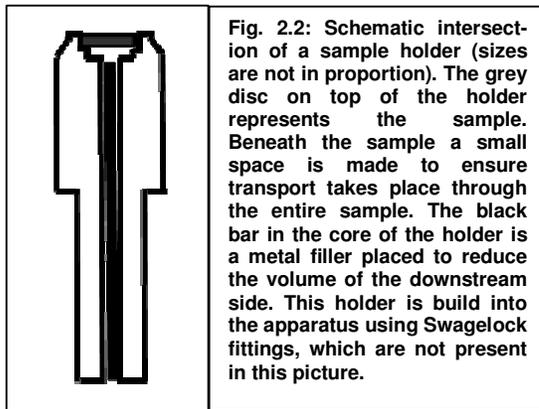


Fig. 2.2: Schematic intersection of a sample holder (sizes are not in proportion). The grey disc on top of the holder represents the sample. Beneath the sample a small space is made to ensure transport takes place through the entire sample. The black bar in the core of the holder is a metal filler placed to reduce the volume of the downstream side. This holder is build into the apparatus using Swagelock fittings, which are not present in this picture.

created pressure gradient causes a flow through the sample and a permeability can be calculated. Although the upstream pressure was never really constant it was made as constant as possible by adding an additional volume of about 20 ml to this side of the apparatus. The downstream volume is kept as small as possible (spaces in the tubes in the downstream side and in the pressure transducer are filled up with steel fillers) to get accurate temperature values.

The pressure transducer on the downstream side was especially designed and constructed because normally these pressure transducers have a relatively large internal volume, while it has to be as small as possible. The pressure transducer contains two sets of strain gauges placed in a Poisson arrangement (circumferential and longitudinal), and are wired in a Wheatstone bridge circuit on a hollow steel cylinder. When the pressure increases the cylinder expands slightly. By placing a steel filler inside this hollow cylinder a sensitive pressure transducer can be created with a very low internal volume. A spacing of only 0.05 mm between the filler and the wall of the transducer exists, which reduces the internal volume of the transducer to about 0.1 ml.

A stainless steel sample holder with an outer diameter of 9 mm was used to store the 6 mm diameter,  $\pm 2$  mm thick disc-shaped sample during the experiments. Furthermore, a small space was created directly beneath the sample (fig. 2.2) with a diameter of about 5 mm and a height of about 1 mm to ensure transport takes place through the entire sample and not only through the centre.

## 2.2 Material Description

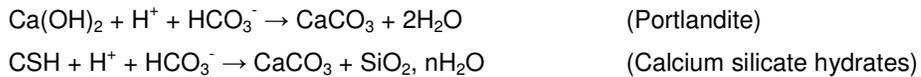
### 2.2.1 Coal samples

The coal samples used in this research are Brzeszcze 364 bituminous coal from Poland. This coal formation was deposited in an intermontane basin during the early Westphalian (Van Bergen et al., 2006) and is one of the six main coal seams present in this area, ranging in thickness between 1 and 3.5 m. The 364 coal seam is a high volatile bituminous coal with a large amount of vitrinite and a vitrinite reflectance of 0.8-0.85% Ro (Wolf et al., 2008). Regionally, this coal has a low to moderate permeability (1-2 mD), which decreases gradually with depth (McCants et al., 2001). During the RECOPOL project (Pagnier et al., 2006) the permeability of seam 364 was already assessed and turned out to be 0.4-1.5 mD. This permeability was measured on relatively large samples containing a cleat system with two main directions, 15° and 105° (Wolf et al., 2008).

### 2.2.2. Cement samples

The type of cement used for this research is ENCI Portland cement class A, which consists for the largest part out of calcium silicate hydrates and portlandite. Also a limited amount of calcium sulfates is present which controls the set time of the cement. A lot of calcium is present in this type of cement and when this calcium reacts with water and supercritical CO<sub>2</sub> the product will be calcite, dolomite and

amorphous silica gel (e.g., Short et al., 2001; Duguid, 2006; Jacquemet et al., 2007; Rimmelé, 2008), according to the following reactions (Brandvoll et al. 2009):



## 2.3 Sample preparation

Two different kind of materials have been used for permeability measurements, coal and cement. The preparation of coal samples was different as for cement samples because of the difference in material properties. In the sections below the preparation process is described for both materials.

### 2.3.1 Coal samples

The coal type used is Brzeszcze 364 bituminous coal from Poland. Samples are disc shaped, with a diameter of roughly 5.9 mm and thicknesses in the range 0.4-2 mm. They were made from cores drilled perpendicular to the layering of the coal. This has been done because permeability perpendicular to the layering is smaller than parallel to the layering (e.g. Li et al., 2004) and can be the limiting factor for the permeability of a coal formation. The research was based on sub-cleat matrix blocks because cleats have a large influence on the permeability, they are distinct fluid pathways and clearly increase the permeability. To obtain permeability data of the coal structure itself, not being affected by cleats, cores had to be drilled in between cleats to produce useful samples.

Because coal has a very low permeability, measurements on a 2 mm thick sample took a relatively long time. That is why the thickness of the samples was reduced to about 0.5 mm on average. However, the sample holder had a 2 mm deep space to store the sample. A 1.6 mm thick porous plate with a significantly higher permeability filled the remaining space behind the coal sample. The main reason for using this porous plate was to support the coal disc so that it can withstand a relatively high  $P_{\text{diff}}$ .

After cutting small discs from the cores these discs were polished to obtain a smooth surface. This was done by hand using p-800 and p-4000 grade silicon carbide polishing papers. The discs were observed under an optical microscope to identify cracks or holes (or other high porosity sites) on the surface of the samples. This ensures no damaged samples were used in the experiments.

After polishing and inspection, the sample is ready to be glued into the sample holder using Agomet P76 epoxy resin. First, some glue was placed on the small step present inside the holder. Then glue was put on the side of the porous plate and it was placed in the holder. Also the side of the coal sample was glued and it was placed in the holder. Finally, glue was placed on top of the holder and covered a small part of the sample. This reduces the effective diameter for transport from 5.9 to about 5 mm. The glue was left to dry for about 24 hours after which the holder containing the sample could be build into the apparatus.

### 2.3.2 Cement samples

Different methods have been used for the preparation of cement samples. As well as for the coal, cores of about 6 mm in diameter were drilled from a larger sample. However, because cement has more strength than coal, discs of about 2 mm thickness could be cut directly from these cores. They

already have a smooth surface and further polishing was not needed. Discs with a thickness of about 2 mm were used in the experiments; it was not necessary to reduce the thickness, as was done for coal samples, because permeability was expected to be high enough to give quick and reliable results. As the samples were thicker a porous plate was not required.

Before the cement samples were glued into the holder they were dried for at least 24 hours in an oven, which keeps a constant temperature of 50 °C. This was done to remove any residual water still present in the sample.

Several prepared cement samples showed leakages during experiments. They were removed from the setup and checked for leaks by placing a droplet of water on top of the sample and force compressed air from beneath through the sample. The leak was indicated by a clear trace of air bubbles. It was not possible to check sample CM12 in this way because it is not glued in the holder and would be blown out when compressed air is forced through.

Several techniques to prepare the samples better and reduce the chance for leakages have been tried. Like narrowing the space between the sample and the steel holder or smearing a layer of resin on the edge of the sample, which fills the pores on the edge, and leave it to dry. However, these techniques did not have the aimed effect.

As gluing the samples in the same manner as described above for the coal samples was problematic, a different technique was used to seal the samples in the holder. Now a small Teflon ring was placed around the sample. On the edge of the sample itself a thin layer of Agomet resin was smeared to smoothen the contact between the sample and the Teflon ring. The diameter of the sample plus Teflon ring was slightly larger than the 6 mm diameter of the space in the holder, so the sample had to be forced into the holder. The Teflon ring now tightly held the sample and closes all possible leaks. This technique was first used on sample CM12 and it seemed to work.

Before starting the experiments the sizes of the cement samples (area and length) have to be determined for further use in the permeability calculations. The effective diameter of sample CM06 was 5.5 mm, which gives an area of  $2.38 \times 10^{-5} \text{ m}^2$ . During later experiments, due to minor repairs, the effective diameter changed to 4.75 mm (an area of  $1.77 \times 10^{-5} \text{ m}^2$ ). The length of the sample was 2.45 mm. The second sample (CM12) had an effective diameter of 5.89 mm, which gives an area of  $2.72 \times 10^{-5} \text{ m}^2$  and a length of 1.95 mm.

The anhydrite sample used for permeametry experiments was prepared in the same way as cement.

### *2.3.3 Sample wetting methods*

In order to investigate the effect of water on the permeability of cement it was necessary to do experiments on wet cement samples. The amount of water present in the sample can have a relatively large influence on the permeability, hence it is important to add sufficient water.

Two different wetting methods have been used to add water. Method 1 was placing a droplet of demineralized water on top of the sample (with the sample already glued into the sample holder), leaving the water on the sample for a few hours to be absorbed, and then removing the remaining water.

As this method might not have resulted in full saturation of the sample, a 2<sup>nd</sup> method was developed. The sample holder containing the sample was put upside down into a glass of demineralized water in

such a way only a small part of the holder (about the thickness of the sample) was under water. This setup was placed in a vacuum chamber and for about half an hour the chamber was evacuated. After the sample was removed from the vacuum chamber the remaining water was removed from the sample.

## 2.4 Experiments

### 2.4.1 Coal experiments

The approach for experiments with coal is slightly different because after evacuating the apparatus and applying pressure again (in this case to 10 MPa) the sample was left under this pressure for about 24 hours, in order to allow the coal to stabilize. It is well known coal swells due to the adsorption and absorption of CO<sub>2</sub>. Radial expansion is prevented because of the 1.5 mm steel wall, but axial expansion can still take place in small amounts. Regardless of the porous plates, the relative fragility of the thin sample discs meant that P<sub>dif</sub> was restricted to 0.5 MPa.

### 2.4.2 Cement experiments

A slightly different approach was needed for experiments on coal compared to those on cement. When the glue on the cement sample was completely dried and after the sample was dried in an oven at ± 50 °C for about 24 hours to remove all residual water (drying only for experiments with dry cement), the samples could be build into the apparatus. First, a pressure of about 5 MPa was applied to the system to check for leaks in the apparatus. When no leaks were present, the pressure was released, after which the apparatus was evacuated to remove air present in the apparatus. Next, the system was re-pressurized to e.g. 5.5 MPa, after which the pressure was reduced to 5 MPa again and valve 6 (fig. 2.1) was closed. To start the experiment the pressure on the upstream side was increased to 5.5 MPa, creating a pressure difference of 0.5 MPa over the sample, and immediately transport starts to take place. Directly at the start of the experiment valve 4 was closed.

## 2.5 Downstream volume calibration

It is important to accurately determine the downstream volume, as this volume is used in the permeability calculations. This volume was calibrated by isolating the downstream side of the system by closing valve 6 (fig. 2.1) and by placing a steel dummy sample in the sample holder. The downstream volume, which is a constant, is calculated with the following formula:

$$\Delta M = V \cdot \Delta \rho$$

Where  $\Delta M$  is the mass of the released CO<sub>2</sub>,  $V$  is the downstream volume, and  $\Delta \rho$  is the change in density due to a decrease in pressure. A CO<sub>2</sub> pressure of about 3.15 MPa was applied to the system. By opening valve 10 (fig. 2.1) gradually a known amount of CO<sub>2</sub> pressure was released from the downstream side and the volume of escaped CO<sub>2</sub> at atmospheric pressure was measured. This was done 5 times to obtain a larger volume of CO<sub>2</sub> from the system. The mass of the released CO<sub>2</sub> can be calculated by using the density (at atmospheric pressure). Due to the release of CO<sub>2</sub> from the downstream side the pressure and density in the system decreased. The decrease in density can be calculated by using the change in pressure and the temperature. This change in density together with

the mass of the released CO<sub>2</sub> makes it possible to calculate the volume of the downstream side, which is a constant, following the equation above.

This measurement was done 5 times to obtain a more accurate value for the downstream volume. As can be seen in table 2.1 the precision of the measurements is relatively high compared to the average volume of 0.977 ml.

Measurement	Volume (ml)
1	0,996
2	0,975
3	0,968
4	0,986
5	0,961

Table 2.1: Downstream volume calibration

## 2.6 Data processing

The pressure and temperature data used for the permeability calculations are logged by a data acquisition system and VI-logger software.

Before each experiment was started the upstream and downstream pressure signals had to be calibrated with the pressure signal indicated by a Keller PAA-33X pressure transducer that is located before the upstream side of the apparatus. After the experiments the downstream pressure signal was about 0.03 MPa higher (caused by the correction of the signal at the start of the experiment) than the upstream pressure while an equal pressure was to be expected at the end of the experiment because flow has stopped at this point and the valve between both sides was opened. Since the upstream pressure still corresponded to the pressure indicated by the Keller transducer, this means the downstream pressure transducer must have a deviation in its signal equivalent to about 0.03 MPa. This deviation has to be taken into account in further calculations. This was done by subtracting a certain amount of pressure from the downstream signal for each 10 second step. From observations turned out that the signal does not instantly deviate 0.03 MPa but gradually increases the deviation from 0 to 0.03 MPa during the experiment. That is why the amount subtracted from the signal was linearly increased starting with 0 MPa at the start of the experiment and ending with 0.03 MPa at the end.

## 2.7 Permeametry method

Permeabilities in this research are calculated with use of a modified transient step permeametry model of Sutherland and Cave (1980). This model assumes an upstream volume with pressure  $P_1$  and volume  $V_1$ , and a much smaller downstream volume with pressure  $P_2 = P_0$  and volume  $V_2$ . However, the downstream volume is still significantly larger than the corrected pore volume of the sample. A transient step is created ( $\Delta P_0 = P_1 - P_0$ , at  $t = 0$ ) and transport takes place through the sample. The formula for the pressure decay can be written as:

$$\Delta p_t = \Delta p_0 e^{-mt} \quad (1)$$

$$|p_1 - p_2|_{t=t} = \Delta p_t \quad (2)$$

$$|p_1 - p_2|_{t=0} = \Delta p_0 \quad (3)$$

$$m = \frac{\kappa A}{\beta \eta l} \left( \frac{V_1 + V_2}{V_1 V_2} \right) = \frac{\kappa A}{\eta l} \left( \frac{1}{\beta V_1} + \frac{1}{\beta V_2} \right) \quad (4)$$

$$\beta = \frac{\Delta V}{V \Delta p} \quad (5)$$

Where  $\kappa$  is the permeability ( $\text{m}^2$ ),  $A$  is the area of the sample ( $\text{m}^2$ ),  $V_1$  is the upstream volume ( $\text{m}^3$ ),  $V_2$  is the downstream volume ( $\text{m}^3$ ),  $\beta$  is the isothermal compressibility ( $1/\text{Pa}$ ),  $\eta$  is the dynamic viscosity ( $\text{Pa}\cdot\text{s}$ ), and  $l$  is the length of the sample ( $\text{m}$ ). For each individual sample  $A$ ,  $V_1$ ,  $V_2$ , and  $l$  are constant values while  $\kappa$ ,  $\beta$ ,  $\eta$  are variable. Now, (5) can be rewritten:

$$\text{For } V_1, \beta V_1 = \frac{\Delta V}{\Delta p} = C_1 \quad (6)$$

$$\text{For } V_2, \beta V_2 = \frac{\Delta V}{\Delta p} = C_2 \quad (7)$$

When taking natural logarithms of (1) the resulting formula is as follows:

$$\ln(\Delta p_t) = \ln(\Delta p_0) - mt \quad (8)$$

The slope of this equation is  $m$  and when filling in (6) and (7) in equation (4) the formula for  $m$  becomes:

$$m = \frac{\kappa A}{(C_1 + C_2) \eta l} \quad (9)$$

From (9) a formula for the permeability can be derived:

$$\kappa = \frac{m(C_1 + C_2) \eta l}{A} \quad (10)$$

As data were logged with 10 sec. intervals, for each 10 second step a permeability can be calculated. Several parameters in (10) change when the pressure changes ( $m$ ,  $C_1$ ,  $C_2$ , and  $\eta$ ) and to obtain an accurate value for the permeability these parameters have to be calculated for each step. The permeabilities given in the tables and graphs (see Results section) are averages of the permeability values of each step in one test. During the first steps of an experiment the calculated permeability was relatively high, but decreased when time elapsed. Differences in permeability between single steps were relatively random, which is the reason why the average of all steps was used to describe the permeability of the sample. The area and length of the samples are constant values.

Values for the dynamic viscosity and isothermal compressibility are calculated using equations of state for  $\text{CO}_2$  and argon. The dynamic viscosity is based on the pressure of the fluid in the sample, but since a pressure gradient is present inside the sample a mean value for the pressure  $((p_1 + p_2)/2)$  is used to calculate the dynamic viscosity. The isothermal compressibility has to be calculated for both the upstream and downstream side.

The dynamic viscosity and isothermal compressibility values of  $\text{CO}_2$  were obtained by using a computer model for the equation of state. The model is an Excel add-in called CO2tables and is produced by MegaWatSoft. The model uses an equation of state presented by Span & Wagner (2003)

and calculates transport properties by using equations presented in the studies of Fenghour et al. (1998) and Vesovic et al. (1990). Pressure and temperature data had to be put in after which the model gives the corresponding values of the dynamic viscosity and isothermal compressibility.

The  $m$  value could be determined by plotting the natural logarithm of the pressure difference against time. To the resulting graph a trend line could be fitted the slope of which represents the  $m$  value. However, to obtain a more accurate result the  $m$  value was calculated for each step using eq. (8).

Now every parameter in (10) can be filled in and the permeability for each step can be calculated. Averaging the permeabilities of all steps gives the permeability for the sample at a certain pressure.

### 3. Results

Boreholes used for the injection of CO<sub>2</sub> in underground reservoirs are commonly sealed with ENCI Portland cement Class A. Transient step permeametry tests were performed on this type of cement to investigate the permeability to CO<sub>2</sub> and argon at different background pressures. Also the effect of water on the permeability has been tested. In this section of the report the experimental results are given. Permeability data of tests on dry and wet cement are given, using both CO<sub>2</sub> and argon. These results will make it possible to conclude if the amount of leakage is significant and how much the presence of water influences the permeability. With use of this information a decision can be made about the further use of this type of cement or if it is necessary to find another way to seal the boreholes.

Experiments have been done on both coal and cement samples. However, CO<sub>2</sub>-permeametry results on coal samples were not obtained as a consequence of difficulties in gluing and sealing the samples. Experiments on cement were performed under both dry and wet conditions to investigate the effect of water on permeability, using both CO<sub>2</sub> and argon. Data of only two samples could be generated (CM06 and CM12) because cement likewise turned out to be difficult to seal into the holder.

#### 3.1 CO<sub>2</sub> experiments

##### 3.1.1 Dry cement

The first cement samples used for testing gave very low permeabilities (of the order  $10^{-19}$  m<sup>2</sup>), much lower than expected (Carey et al., 2007; Liteanu, 2009). The samples were then dried, this resulted in considerably higher permeabilities. Therefore, dry experiments were done as well as wet experiments to investigate the effect of water. To exclude a permanent lowering of the permeability, possibly caused by water, all experiments on dry samples were performed before the wet experiments.

For each pressure (5.5, 7.5, 10, 12.5, and 15 MPa), three or more experiments were performed to obtain a more accurate value for the permeability. This was done for both samples and the results are described below.

##### Sample CM06

The first experiments on sample CM06 were done with a background pressure of 5.5 MPa. The sample was kept pressurized between experiments and overnight at the background pressure. An overview of the performed experiments with the resulting permeabilities and additional information can

be found in table 3.1 and 3.2. With only a few exceptions lower permeabilities are measured at higher background pressures. The exceptions include the two tests at 7.5 MPa ( $P_1$ ) using a pressure difference ( $P_{dif}$ ) of 1.0 Mpa (test 7 & 8). These tests gave significantly lower permeabilities than the tests at 7.5 MPa using a  $P_{dif}$  of 0.5 MPa. Another deviation of the decreasing trend was test 11, which showed a slightly higher permeability than those of the 10 MPa tests performed earlier. Another test at 5.5 MPa was done to check the sample for leaks. This test showed a much lower permeability than before. Also the first two experiments at 15 MPa give higher permeabilities than the results of the 15 MPa test performed a day before. The last two tests in the table represent data of the same sample after experiments at wet conditions were performed. Before testing the sample was dried again, this was done to investigate the possible permanent effect of water on the permeability of cement. The first of these two tests shows clearly a much lower permeability at a 5.5 MPa pressure. The second one does not, but there was a leak in the sample during this test.

The negative trend described above can be observed when plotting the permeability against the background pressure. Only the results of the 7.5 MPa test using a  $P_{dif}$  of 1.0 MPa are left out. This shows permeability is clearly decreasing with increasing pressure (fig. 3.1).

Test	$P_1$ (MPa)	$P_2$ (MPa)	$P_{dif}$ (MPa)	Permeability ( $m^2$ )	Date	Extra info
1	5,5	5,0	0,5	2,82E-16	4-3-2009	CM06 installed + evacuated
2	5,6	5,1	0,5	3,00E-16	4-3-2009	
3	5,6	5,0	0,6	3,08E-16	4-3-2009	
4	7,5	7,0	0,5	2,42E-16	4-3-2009	
5	7,5	7,0	0,5	2,20E-16	4-3-2009	
6	7,5	7,0	0,5	1,98E-16	4-3-2009	
7	7,5	6,5	1,0	7,39E-17	4-3-2009	
8	7,5	6,5	1,0	7,04E-17	4-3-2009	
9	10,0	9,5	0,5	1,45E-16	4-3-2009	
10	10,2	9,5	0,7	1,52E-16	4-3-2009	
11	10,1	9,5	0,6	1,88E-16	5-3-2009	CO2 during night
12	5,5	5,0	0,5	7,78E-17	5-3-2009	
13	12,4	11,9	0,5	1,11E-16	5-3-2009	
14	12,7	12,0	0,7	1,11E-16	5-3-2009	
15	12,6	12,0	0,6	1,06E-16	5-3-2009	
16	12,6	11,5	1,1	1,05E-16	5-3-2009	
17	10,1	9,5	0,6	1,36E-16	5-3-2009	
18	15,0	14,3	0,7	9,20E-17	5-3-2009	
19	15,0	14,5	0,5	9,80E-17	6-3-2009	CO2 during night
20	15,0	14,3	0,7	9,58E-17	6-3-2009	CM06 removed
21	5,5	5,0	0,5	6,54E-17	14-4-2009	CM06 installed
22	5,5	5,0	0,5	1,86E-16	14-4-2009	Leak! CM06 removed

Table 3.1: All permeametry experiments performed for sample CM06 under dry conditions using CO<sub>2</sub>.

$P_1$ (MPa)	$P_2$ (MPa)	$P_{dif}$ (MPa)	Mean permeability ( $m^2$ )
5,5	5,0	0,5	2,42E-16
7,5	7,0	0,5	2,20E-16
7,5	6,5	1,0	7,22E-17
10,0	9,5	0,5	1,55E-16
12,5	12,0	0,5	1,10E-16
12,6	11,5	1,1	1,05E-16
15,0	14,5	0,5	9,53E-17

Table 3.2: Mean permeabilities of CO<sub>2</sub> experiments performed per pressure range for sample CM06 under dry conditions.

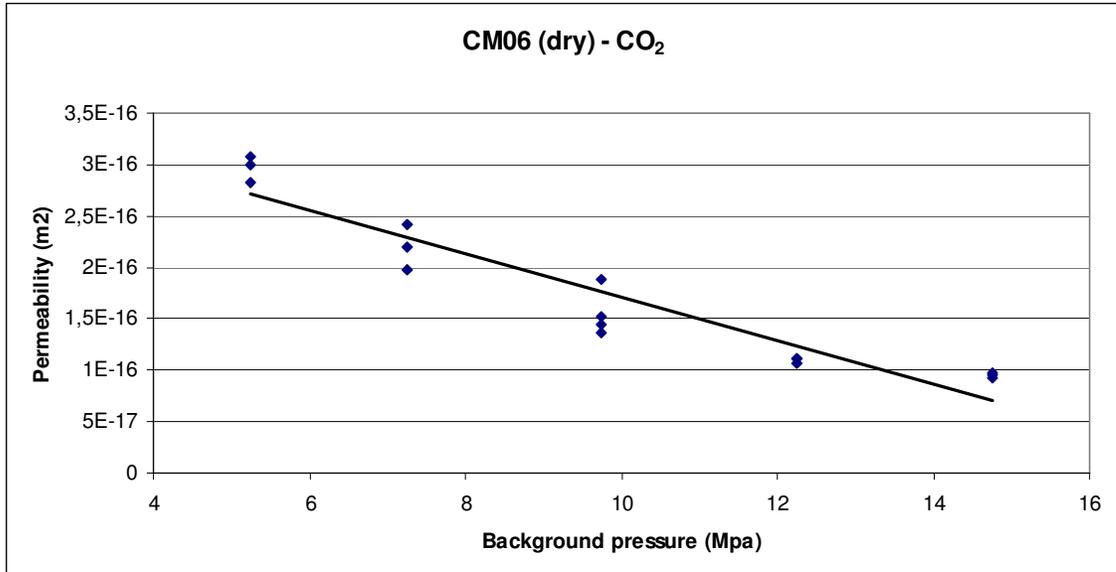


Fig. 3.1: Mean permeabilities of sample CM06 under dry conditions using CO<sub>2</sub> plotted against the mean pressure with a negative trend line added. Data points of tests with 10 MPa differential pressure are not plotted here.

Sample CM12

The permeability data of sample CM12 are given in table 3.3 and 3.4. Measured permeabilities reproduce quite well, and do not depend strongly on the background pressure. Only a slight increase in permeability can be observed from 5.5 MPa to 10 MPa, and with further increasing pressure permeability slightly decreases again. This trend is shown in figure 3.2 where the mean permeability is plotted against the background pressure.

Test	P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>dif</sub> (MPa)	Permeability (m <sup>2</sup> )	Date	Extra Info
1	5,5	5,0	0,5	1,78E-16	9-6-2009	Sample installed + evacuated
2	5,5	5,0	0,5	1,72E-16	9-6-2009	
3	0,5	5,0	0,5	2,08E-16	9-6-2009	
4	7,5	7,0	0,5	2,28E-16	9-6-2009	
5	7,5	7,0	0,5	2,11E-16	9-6-2009	
6	7,5	7,0	0,5	2,17E-16	9-6-2009	CO2 during night
7	10,0	9,5	0,5	3,05E-16	10-6-2009	
8	10,0	9,5	0,5	3,34E-16	10-6-2009	
9	10,0	9,5	0,5	3,47E-16	10-6-2009	
10	12,5	12,0	0,5	2,74E-16	10-6-2009	
11	12,5	12,0	0,5	2,67E-16	10-6-2009	
12	12,5	12,0	0,5	2,66E-16	10-6-2009	
13	15,0	14,5	0,5	2,35E-16	10-6-2009	
14	15,0	14,5	0,5	2,50E-16	10-6-2009	
15	15,0	14,5	0,5	2,38E-16	10-6-2009	Sample removed

Table 3.3: All permeametry experiments performed for sample CM12 under dry conditions using CO<sub>2</sub>.

P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>dif</sub> (MPa)	Mean Permeability (m <sup>2</sup> )
5,5	5,0	0,5	1,86E-16
7,5	7,0	0,5	2,19E-16
10,0	9,5	0,5	3,29E-16
12,5	12,0	0,5	2,69E-16
15,0	14,5	0,5	2,41E-16

Table 3.4: Mean permeabilities of the CO<sub>2</sub> experiments performed per pressure range for sample CM12 under dry conditions.

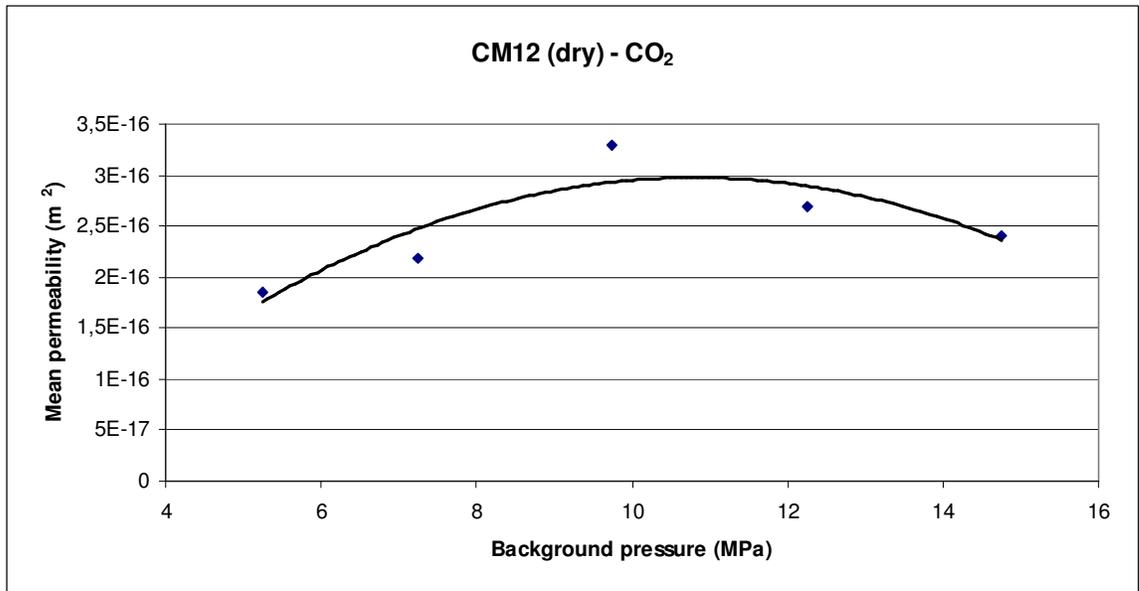


Fig. 3.2: Mean permeabilities to CO<sub>2</sub> for sample CM12 under dry conditions plotted against the pressure. The trend in this case is not linear but has a parabolic shape.

### 3.1.2 Wet cement

Experiments using CO<sub>2</sub> on wet cement were performed last because of the possible chemical reaction of CO<sub>2</sub> with water and calcium in the cement.

#### Sample CM06

After evacuating the apparatus experiments were started, again from low pressure to high pressure. The results of sample CM06 are given in table 3.5 and 3.6. On the first day three experiments at 5.5 MPa (test 1-3) and two on 7.5 MPa (test 4 & 5) were performed. Test 1-3 show a quite distinguished drop in permeability, going from  $5.84 \times 10^{-17}$  for test 1 to  $4.61 \times 10^{-17} \text{ m}^2$  for test 3. At 7.5 MPa the decrease in permeability continued. On the end of the day pressure was released to prevent chemical reactions to take place during the night. The sample was not removed from the apparatus. The next day the apparatus was evacuated again and three experiments at 10 MPa (test 6, 7 and 10) and two at 12.5 MPa (test 8 & 9) were performed. The experiments gave a much higher permeability compared with tests run on the previous day. However, again a decrease in permeability takes place from test 6 to 7 and from 8 to 9. Test 10 has a permeability similar to those of test 6 and 7. The sample was removed after test 10 because there was a leak in the sample.

Test 11 and 12 were performed a week later after the leak was sealed. The purpose of these tests was to investigate the effect of aging, which means leaving the wet sample under pressure for a longer time in order to investigate if any chemical reaction takes place and reduces the permeability. Test 11 was done after 24 hours and test 12 after 48 hours of CO<sub>2</sub> pressure on the sample, both at 5.5 MPa. The resulting permeabilities are similar to each other and only slightly smaller than the permeabilities of test 1-3.

By plotting the mean permeability against the background pressure it becomes clear there is an obvious step in the results between the first and second day. Permeabilities on the same day show a

slight decrease with increasing pressure, but there is a large difference between the permeabilities of 5.5 and 7.5 MPa performed on the first day and those of 10 and 12.5 MPa performed on the second day (fig. 3.3).

Data of CO<sub>2</sub> experiments on wet cement for sample CM12 are lacking due to apparatus issues in a late stadium of the research.

Test	P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>dif</sub> (MPa)	Permeability (m <sup>2</sup> )	Extra info
1	5,5	5,0	0,5	5,84E-17	Wetted + CM06 installed + evacuated
2	5,5	5,0	0,5	5,30E-17	
3	5,5	5,0	0,5	4,61E-17	
4	7,5	7,0	0,5	4,97E-17	
5	7,5	7,0	0,5	4,20E-17	Released P at end of day, not removed
6	10,0	9,5	0,5	1,32E-16	Evacuated
7	10,0	9,5	0,5	1,11E-16	
8	12,5	12,0	0,5	1,09E-16	
9	12,5	12,0	0,5	1,07E-16	
10	10,0	9,5	0,5	1,26E-16	CM06 removed
					Wetted + CM06 installed + evacuated
11	5,5	5,0	0,5	4,58E-17	55 bar CO2 pressure overnight
12	5,5	5,0	0,5	4,60E-17	55 bar CO2 pressure overnight + removed

Table 3.5: All permeametry experiments performed for sample CM06 under wet conditions using CO<sub>2</sub>.

P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>dif</sub> (MPa)	Mean Permeability (m <sup>2</sup> )
5,5	5,0	0,5	5,25E-17
7,5	7,0	0,5	4,58E-17
10,0	9,5	0,5	1,23E-16
12,5	12,0	0,5	1,08E-16

Table 3.6: Mean permeabilities of CO<sub>2</sub> experiments performed per pressure range for sample CM06 under wet conditions.

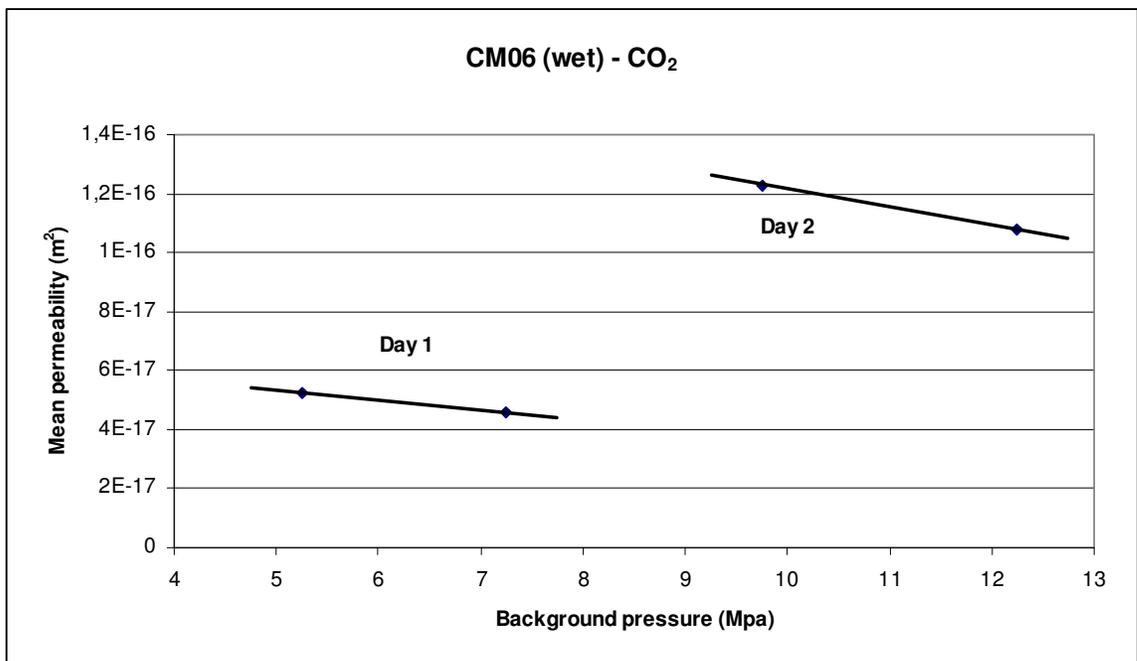


Fig. 3.3: Mean permeabilities to CO<sub>2</sub> for sample CM06 under wet conditions plotted against the pressure. Although it is the same sample two distinct negative trends can be recognized in these data, which is remarkable.

Now a comparison can be made between the wet and dry results of sample CM06 using CO<sub>2</sub> (fig. 3.4). Clearly the low pressure results of wet cement have a significantly lower permeability than those for dry cement, while the high pressure permeabilities of wet cement are very close the dry cement permeabilities.

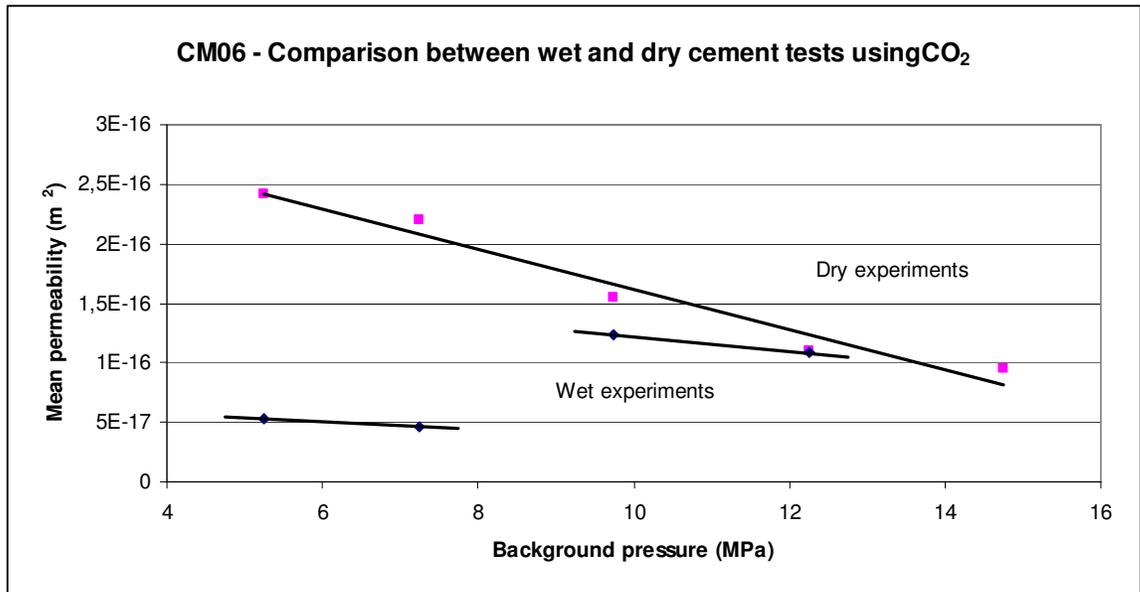


Fig. 3.4: Comparison between wet and dry cement permeametry experiments for sample CM06 using CO<sub>2</sub>. A significant difference in permeability is present between the wet and dry data.

## 3.2 Argon experiments

### 3.2.1 Dry cement

In addition to CO<sub>2</sub> permeabilities, argon permeabilities were also determined to make a comparison. Permeabilities are expected to be similar, since permeability is a material property and does not depend on the fluid or gas used for flow measurements. However, the possible occurrence of the Klinkenberg effect (Klinkenberg, 1941) can produce different permeabilities for different gases. Argon experiments on dry cement were performed after the dry CO<sub>2</sub> experiments, but before the wet experiments on the same samples. Again three tests for each pressure have been done to obtain a more accurate result.

#### Sample CM06

Test results of sample CM06 are given in table 3.7 and 3.8. The first three tests were done at 5.5 MPa and show a relatively high permeability compared with the rest of data. After the third test there was clear evidence for a leak in the sample. This leak was sealed by placing a thin layer of glue around the edge of the sample, leading to a decrease in the effective diameter of the sample. Experiments at 7.5 and 10 MPa were done on one day and all measured permeabilities were similar to each other. After leaving the sample under pressure during the night, the next day experiments at 12.5 and 15 MPa were done and these also gave similar permeabilities as for test 4 to 9. Finally, another

test at 5.5 MPa was performed giving a much lower permeability than the previous 5.5 MPa tests, more in line with the other test results.

The mean permeability against background pressure plot (fig. 3.5) for argon on dry cement shows that permeability does not change with pressure. Only at 5.5 MPa there are some variations in the measurements.

Test	P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>dif</sub> (MPa)	Permeability (m <sup>2</sup> )	Date	Extra info
1	5,5	5,0	0,5	2,85E-17	9-3-2009	CM06 installed + evacuated
2	5,5	5,0	0,5	2,79E-17	9-3-2009	
3	5,5	5,0	0,5	4,04E-17	9-3-2009	CM06 removed
4	7,5	7,0	0,5	1,79E-17	18-3-2009	CM06 installed + evacuated
5	7,5	7,0	0,5	1,85E-17	18-3-2009	
6	7,5	7,0	0,5	1,80E-17	18-3-2009	
7	10,0	9,5	0,5	1,73E-17	18-3-2009	
8	10,0	9,5	0,5	1,83E-17	18-3-2009	
9	10,0	9,5	0,5	1,72E-17	18-3-2009	
10	12,5	12,0	0,5	1,65E-17	19-3-2009	Ar pressure during night
11	12,5	12,0	0,5	1,76E-17	19-3-2009	
12	12,5	12,0	0,5	1,67E-17	19-3-2009	
13	15,0	14,5	0,5	1,73E-17	19-3-2009	
14	15,0	14,5	0,5	1,85E-17	19-3-2009	
15	15,0	14,5	0,5	1,65E-17	19-3-2009	
16	5,5	5,0	0,5	1,84E-17	19-3-2009	CM06 removed

Table 3.7: All permeametry experiments performed for sample CM06 under dry conditions using argon.

P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>dif</sub> (MPa)	Mean Permeability (m <sup>2</sup> )
5,5	5,0	0,5	2,88E-17
7,5	7,0	0,5	1,81E-17
10,0	9,5	0,5	1,76E-17
12,5	12,0	0,5	1,69E-17
15,0	14,5	0,5	1,74E-17

Table 3.8: Mean permeabilities of argon experiments performed per pressure range for sample CM06 under dry conditions.

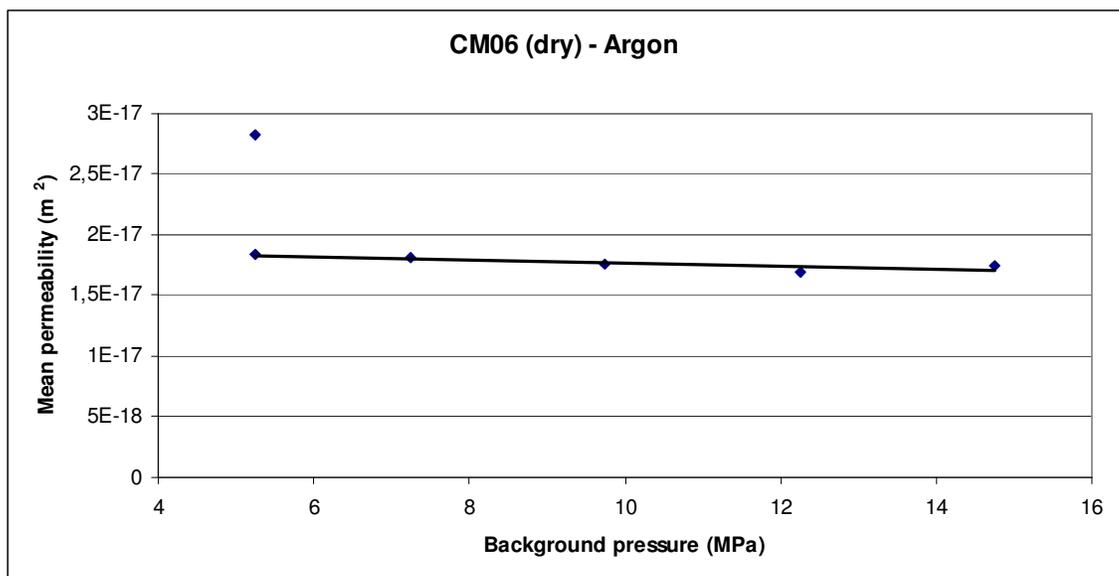


Fig. 3.5: Mean permeabilities to argon for sample CM06 under dry conditions plotted against the pressure. The permeabilities of the four highest pressure ranges are nearly equal while at 5.0 MPa the permeability is significantly higher. This is remarkable and will be discussed later.

Sample CM12

Argon experiments were also performed on sample CM12 (table 3.9 and 3.10). Striking differences in permeability can be observed between sample CM06 and CM12. The permeability of sample CM12 is about 4 times higher than for sample CM06. Furthermore, where differences between permeability values for a similar pressure were relatively small for CM06, they are relatively large for CM12, and a clear positive trend can be recognized in the permeability versus pressure data (fig. 3.6).

Test	P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>diff</sub> (MPa)	Permeability (m <sup>2</sup> )	Date	Extra Info
1	5,5	5,0	0,5	7,90E-17	11-6-2009	CM12 installed + evacuated
2	5,5	5,0	0,5	7,95E-17	11-6-2009	
3	5,5	5,0	0,5	7,54E-17	11-6-2009	
4	7,5	7,0	0,5	7,86E-17	11-6-2009	
5	7,5	7,0	0,5	8,03E-17	11-6-2009	
6	7,5	7,0	0,5	7,33E-17	11-6-2009	
7	10,0	9,5	0,5	8,05E-17	11-6-2009	
8	10,0	9,5	0,5	7,97E-17	11-6-2009	
9	10,0	9,5	0,5	8,06E-17	11-6-2009	
10	12,5	12,0	0,5	7,82E-17	11-6-2009	
11	12,5	12,0	0,5	8,14E-17	11-6-2009	
12	12,5	12,0	0,5	8,43E-17	11-6-2009	
13	15,0	14,5	0,5	8,23E-17	11-6-2009	
14	15,0	14,5	0,5	8,59E-17	11-6-2009	
15	15,0	14,5	0,5	8,11E-17	11-6-2009	
16	5,5	5,0	0,5	7,16E-17	11-6-2009	CM12 removed

Table 3.9: All permeametry experiments performed for sample CM12 under dry conditions using argon.

P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>diff</sub> (MPa)	Mean permeability (m <sup>2</sup> )
5,5	5,0	0,5	7,64E-17
7,5	7,0	0,5	7,74E-17
10,0	9,5	0,5	8,03E-17
12,5	12,0	0,5	8,13E-17
15,0	14,5	0,5	8,31E-17

Table 3.10: Mean permeabilities of argon experiments performed per pressure range for sample CM12 under dry conditions.

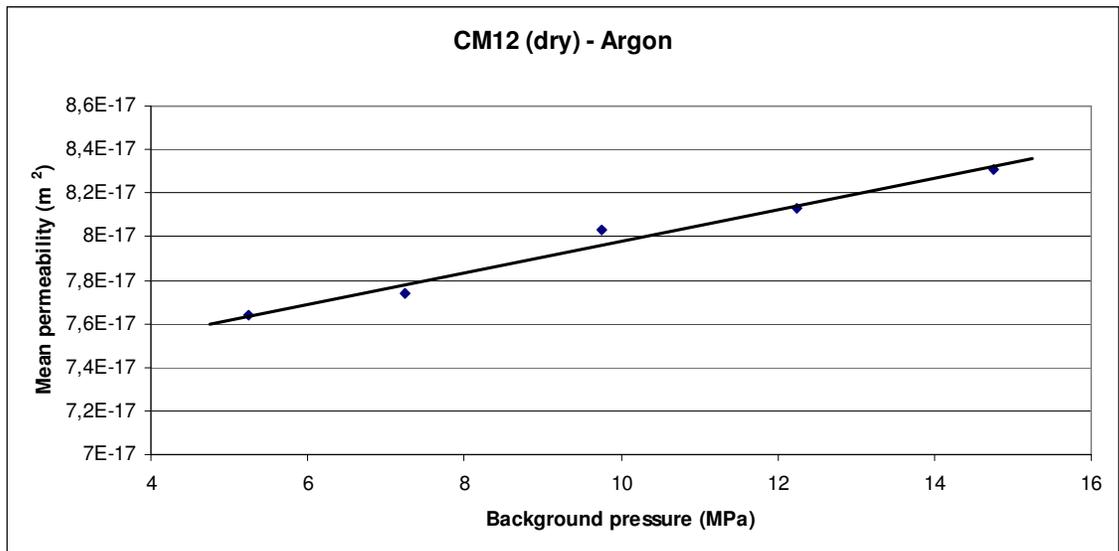


Fig. 3.6: Mean permeabilities to argon for sample CM12 under dry conditions plotted against the pressure. Just as for the argon experiments on dry sample CM06 permeabilities are nearly equal, only a slightly positive trend is present.

### 3.2.2 Wet cement

Argon tests on wet cement were performed before tests with CO<sub>2</sub> on wet cement to avoid a possible permanent decrease in permeability by a chemical reaction again, and to measure the true permeability.

#### Sample CM06

The test results of CM06 on the first day show a relatively constant value for the permeability for all pressures used (table 3.11 and 3.12). The sample was taken out of the apparatus after the first day and was wetted again the next day before installing it into the apparatus again. Surprisingly permeabilities are significantly lower on the second day after the sample was wetted again. Values for the permeability are again relatively constant, but still a clear difference is present between permeabilities of tests 1-8 and tests 9-14. This is especially clear when comparing test 8 (performed at 12.5 Mpa) with tests 9 and 10 (also performed at 12.5 MPa). Permeabilities of 9 and 10 are significantly lower; this can also be recognized in the results of the 10 MPa tests. Tests 13 and 14, which were done a day later, also have clearly lower permeabilities than those of tests 6 and 7.

On the end of the second day the sample was left under 5.5 MPa pressure to investigate the effect of aging. The next day another test showed aging had no effect. The permeability agreed well with the other 5.5 MPa measurements.

Test	P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>dif</sub> (MPa)	Permeability (m <sup>2</sup> )	Data	Extra info
1	5,5	5,0	0,5	1,73E-17	24-3-2009	Wetted + CM06 installed + evacuated
2	5,5	5,0	0,5	1,94E-17	24-3-2009	
3	5,5	5,0	0,5	1,72E-17	24-3-2009	
4	7,5	7,0	0,5	1,59E-17	24-3-2009	
5	7,5	7,0	0,5	1,63E-17	24-3-2009	
6	10,0	9,5	0,5	1,94E-17	24-3-2009	
7	10,0	9,5	0,5	1,65E-17	24-3-2009	
8	12,5	12,0	0,5	1,94E-17	24-3-2009	
9	12,5	12,0	0,5	8,69E-18	25-3-2009	Removed+w etted+installed+evacuated
10	12,5	12,0	0,5	8,56E-18	25-3-2009	
11	15,0	14,5	0,5	8,97E-18	25-3-2009	
12	15,0	14,5	0,5	9,61E-18	25-3-2009	
13	10,0	9,5	0,5	9,32E-18	25-3-2009	
14	10,0	9,5	0,5	9,05E-18	25-3-2009	Ar pressure during night
					26-3-2009	CM06 removed - aging had no effect

Table 3.11: All permeametry experiments performed for sample CM06 under wet conditions using argon.

P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>dif</sub> (MPa)	Mean permeability (m <sup>2</sup> )
5,5	5,0	0,5	1,80E-17
7,5	7,0	0,5	1,61E-17
10,0	9,5	0,5	1,36E-17
12,5	12,0	0,5	1,22E-17
15,0	14,5	0,5	9,29E-18

Table 3.12: Mean permeabilities of argon experiments performed per pressure range for sample CM06 under wet conditions.

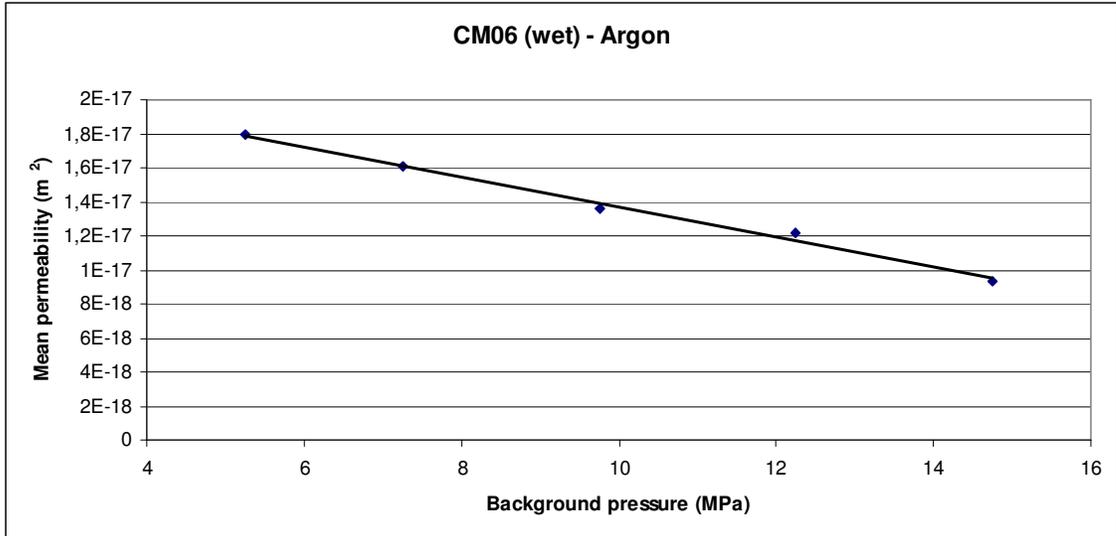


Fig. 3.7: Mean permeabilities to argon for sample CM06 under wet conditions plotted against the mean pressure. A clear negative trend can be observed in the data.

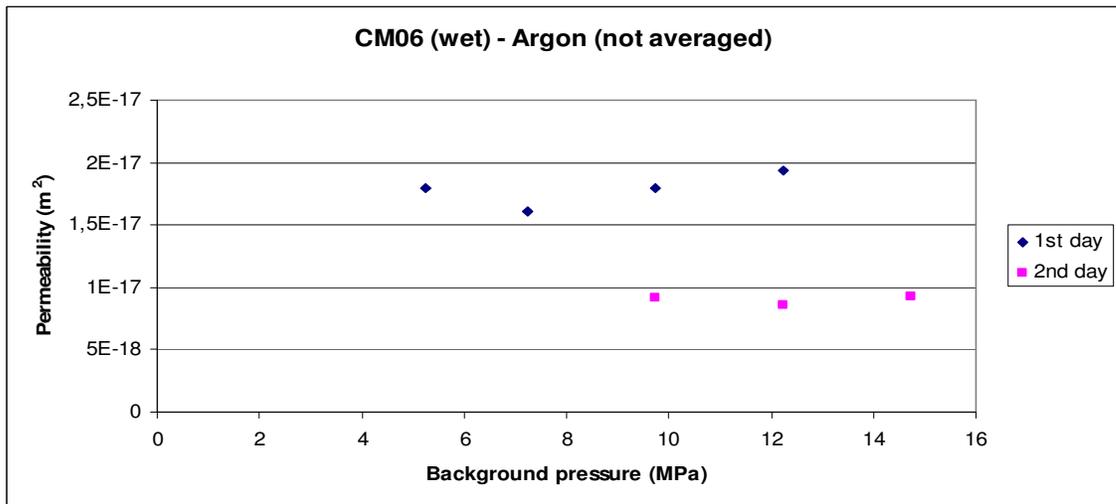


Fig. 3.8: Permeabilities to argon for sample CM06 under wet conditions plotted against the pressure. A difference can be observed between permeabilities measured on the same sample, at similar pressures on the first day and those measured a day later.

Despite the relatively constant permeability a decrease in permeability with increasing pressures can be recognized when plotting the mean permeability against the background pressure (fig. 3.7). This is due to averaged values of the permeability used in the graph and because of that the negative trend in this plot is an artificial effect and does not represent the actual trend. High permeabilities of the first day average out against lower permeabilities of the second day, but this only counts for the 9.5-10.0 and 12.0-12.5 MPa pressure ranges. A second graph is given (fig. 3.8) with non-averaged permeability data. A clear difference is present between permeabilities measured the first day and the second day.

When comparing the permeability results of sample CM06 under wet conditions with the results for dry conditions it turns out wet cement has lower permeabilities, although the difference is not very large, especially for lower pressures (fig. 3.9). The difference between the results at higher pressures is more distinguished.

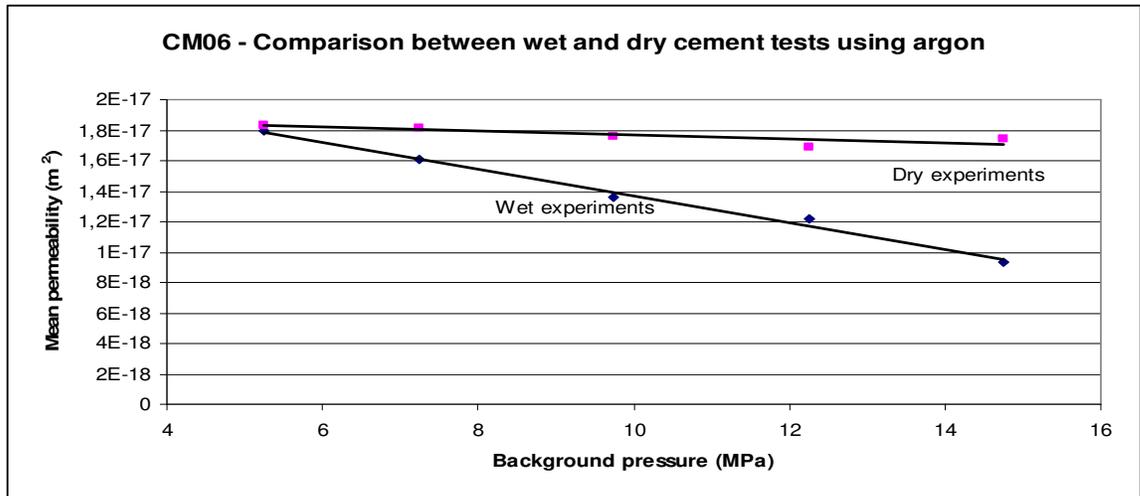


Fig. 3.9: Comparison between wet and dry cement permeametry tests for sample CM06 using argon. The difference between wet and dry permeabilities becomes larger with increasing pressure. This is probably caused by the large difference between low and high pressure results from the wet cement, which are averaged out in this graph.

Sample CM12

Permeabilities measured for sample CM12 are obviously higher than those for CM06 (table 3.13 and 3.14). This is in line with the results of the previous CO<sub>2</sub> and argon permeametry measurements.

Although all permeabilities are in a very close range to each other a slight increase in permeability can be observed when pressure is increased from 5.5 to 10 MPa. Further increasing the pressure again lowers the permeability slightly. After nine tests pressure was released from the apparatus and the next day the sample was wetted again before measurements continued. While this rewetting had a relatively large effect on the measurements for sample CM06, hardly any change in the measurements of sample CM12 can be observed. Figure 3.10 shows the mean permeability plotted against the background pressure and displays the slight trend in the results, which has been described above.

When comparing the results of the wet cement experiments with the dry cement experiments using argon (fig. 3.11) it becomes clear that permeabilities are lower for wet experiments. The difference is not large, but still significant.

Test	P <sub>1</sub> (MPa)	P <sub>2</sub> (MPa)	P <sub>diff</sub> (MPa)	Permeability (m <sup>2</sup> )	Date	Extra Info
1	5,5	5,0	0,5	5,92E-17	15-6-2009	CM12 wetted + installed + evacuated
2	5,5	5,0	0,5	5,23E-17	15-6-2009	
3	5,5	5,0	0,5	5,58E-17	15-6-2009	
4	7,5	7,0	0,5	5,74E-17	15-6-2009	
5	7,5	7,0	0,5	5,77E-17	15-6-2009	
6	7,5	7,0	0,5	5,88E-17	15-6-2009	
7	10,0	9,5	0,5	5,93E-17	15-6-2009	
8	10,0	9,5	0,5	5,89E-17	15-6-2009	
9	10,0	9,5	0,5	5,93E-17	15-6-2009	
10	12,5	12,0	0,5	5,77E-17	16-6-2009	Removed + wetted + installed + evacuated
11	12,5	12,0	0,5	5,81E-17	16-6-2009	
12	12,5	12,0	0,5	5,66E-17	16-6-2009	
13	15,0	14,5	0,5	5,24E-17	16-6-2009	
14	15,0	14,5	0,5	5,60E-17	16-6-2009	
15	15,0	14,5	0,5	5,32E-17	16-6-2009	CM12 removed

Table 3.13: All permeametry experiments performed for sample CM12 under wet conditions using argon.

$P_1$ (MPa)	$P_2$ (MPa)	$P_{diff}$ (MPa)	Mean Permeability ( $m^2$ )
5,5	5,0	0,5	5,58E-17
7,5	7,0	0,5	5,80E-17
10,0	9,5	0,5	5,92E-17
12,5	10,0	0,5	5,75E-17
15,0	14,5	0,5	5,39E-17

Table 3.14: Mean permeabilities of argon experiments performed per pressure range for sample CM12 under wet conditions.

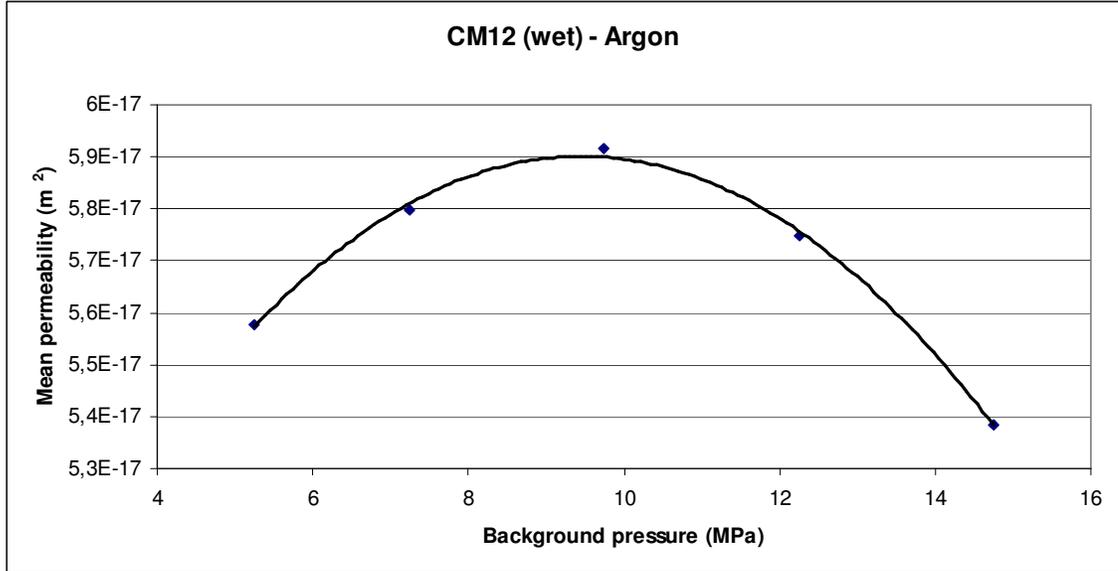


Fig. 3.10: Mean permeabilities to argon for sample CM12 under wet conditions plotted against the pressure. Remarkable is the parabolic trend of the permeability data in this case, which is not expected but corresponds to the  $CO_2$  test data for sample CM12 under dry conditions.

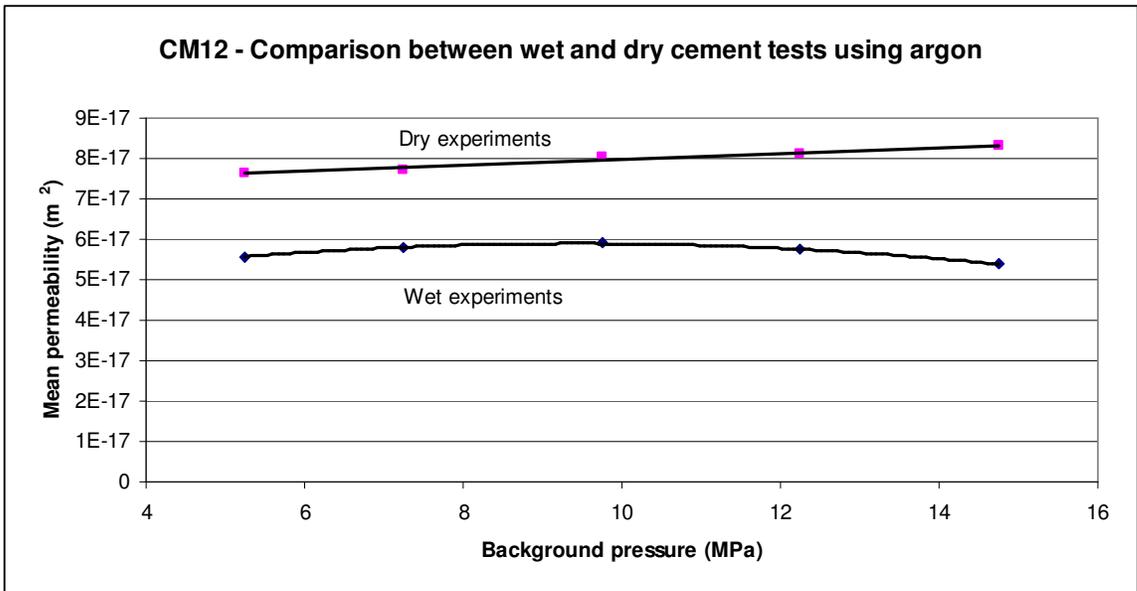
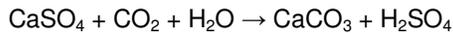


Fig. 3.11: Comparison between wet and dry cement permeametry tests for sample CM12 using argon. The dry experiments have clearly higher permeabilities. Furthermore, the trend of both series is different; linear for the dry experiments and more parabolic for the wet experiments.

### 3.3 Anhydrite experiments

Besides the experiments on coal and cement also one sample of anhydrite was tested in the apparatus. The anhydrite sample was of the same size as the cement samples. A pressure difference of 0.5 MPa was applied to the apparatus with a background pressure of 5.5 MPa. The first test took about a week to reduce the pressure difference to 0 MPa. A second test was done and during this test fluid transport halted while a pressure difference of about 0.2 MPa was still present. So, during the experiment transport became entirely blocked. As well as the first cement samples this anhydrite was not dried before testing, and it is likely that significant amounts of calcite have precipitated.



## 4. Discussion

This research investigates the permeability of ENCI Portland Class A cement, which is the most commonly used type of cement to seal old hydrocarbon reservoirs. The recent interest in the sequestration of CO<sub>2</sub> requires accurate permeability data of this type of cement. When permeabilities turn out to be relatively high significant amounts of gas can possibly escape via these boreholes from the reservoirs and cause high risks in the areas near boreholes. Transient step permeametry tests have been performed to obtain information about the gas-permeability of this type of cement, how this changes with depth, and what the effect of water is. In this section the results of these tests will be compared and discussed. Furthermore, the discussion will focus on whether reconsideration or modification of well-bore sealing techniques is required.

### 4.1 Coal experiments

Permeametry measurements on coal samples were attempted, but were unsuccessful. The main cause for this was the fragility of the thin discs, which were easily broken or damaged. In addition, intact samples generally showed no or hardly any fluid transport during experiments. There are a few possible reasons that could explain this. First, the problem could be the resin used to glue the sample into the holder. When too much resin is used it possibly spreads out beneath the sample when the sample is pushed into the holder, and blocks the fluid pathway. To overcome this less resin was used and later samples are pushed into the holder with more care to prevent the possible spreading of the resin. However, experiments still did not show any fluid transport after this adaptation.

A second reason could be the polishing process. After the samples are roughly polished to the right thickness a finer grade paper is used to make the sample surface smooth. It is possible the fine material removed from the surface ends up in the pores at the uppermost layer of the sample and creates an impermeable zone. A solution can be the use of a laser to polish the surface of the sample. In that case the material is directly removed and does not get the chance to fill the pores in the top layer. However, this method has not been tested yet.

Another explanation for the blocked transport could be swelling of the coal. Coal swells due to absorption and adsorption of CO<sub>2</sub> and in this case the sample cannot expand radially because of the steel wall along the sample. This probably causes the pores in the sample to close because if the coal cannot expand it tends to fill the internal pore space. A possible solution is to start an experiment

directly after it is exposed to CO<sub>2</sub>, but in that case swelling probably takes place during the experiment, which is not desirable. As a workable solution to this problem was not found research was continued on borehole cement.

## 4.2 Cement experiments

### 4.2.1 CO<sub>2</sub> experiments

#### Dry samples

The results of sample CM06 showed that the permeability decreases with increasing pressure (fig. 3.1, table 3.1 and 3.2). However, there were some exceptions. Two experiments performed at 7.5 MPa background pressure using a P<sub>diff</sub> of 1.0 MPa (test 7 & 8) gave significantly lower permeabilities than three other experiments at 7.5 MPa using a P<sub>diff</sub> of 0.5 MPa (test 4-6). This same difference can not be recognized in the results of tests 13-16, where a background pressure of about 12.6 MPa and also a P<sub>diff</sub> of 1.0 MPa (16) and 0.5 MPa (13-15) is used. The permeability does not depend on the pressure difference applied to a sample. This makes the result of test 16 more reliable than those of test 7 & 8. An explanation for the lower permeabilities of test 7 & 8 has not been found. Furthermore, test 12 is performed at exactly the same conditions as test 1-3, but has a lower permeability. Test 12 was performed a day later, but this is unlikely to be the reason for the difference in permeability because CO<sub>2</sub> pressure was kept on the system overnight and should be very stable the next day. The permeability can also be lowered by a chemical reaction taking place during the night, blocking pores in the sample. However, experiments performed later that day gave expected results, which make this hypothesis unlikely.

Sample CM06 was dried, after wet experiments were performed, and tested again at 5.5 MPa. The resulting permeability was significantly lower than the 5.5 MPa tests performed earlier. This is a strong indication for a permanently reduced permeability, probably caused by the wet experiments using CO<sub>2</sub>.

While a decrease in permeability with increasing background pressure would be expected, the results of sample CM12 show an increase in permeability from 5.5 to 10 MPa. At higher pressures the permeability decreases again. It was not possible to check this sample for leaks, but if this was due to a leak permeability would keep increasing, and not decrease again for pressures higher than 10 MPa. The highest permeabilities of sample CM12 were measured at the start of the second day at 10 MPa. The results of sample CM06 also show high permeabilities at the start of a new day, but the difference is not as large as for sample CM12. It remains unclear why the permeability of sample CM12 increases with increasing pressure.

#### Wet samples

The wet experiments on sample CM06 are performed in two days. Remarkably, permeabilities measured during the second day are significantly larger than those measured the first day (fig. 3.3). This can probably be explained by a lack of water in the sample during the second day. At the start of day 2 the sample was not wetted again because it was expected to be still wet. But during the night water probably evaporated, which was possible because the pressure was released from the system.

Permeabilities measured the second day approach the permeabilities measured when the sample was completely dry, as is shown in figure 3.4.

However, permeabilities measured on the same day show the expected trend, a decreasing permeability with increasing background pressure.

Tests 11 and 12 in table 3.5 were performed to investigate the effect of water. If dissolution and precipitation takes place due to the presence of water, CO<sub>2</sub> and calcium, and blocks the pores in the sample, the permeability would decrease with time. Leaving a wet sample pressurized at 5.5 MPa CO<sub>2</sub> pressure for 24 hours gives a slightly lower permeability than at dry conditions and also after 48 hours the permeability did not change. This would not be expected when a chemical reaction causes the lowered permeability. However, if an insufficient amount of water is present in the sample no further dissolution and precipitation can occur and the permeability will not decrease any further. This is probably the reason why the permeability of tests 11 and 12 are similar and much lower than at dry conditions.

#### 4.2.2 Argon experiments

##### Dry samples

During the third experiment at 5.5 MPa using sample CM06 a leak was discovered. After the sample was repaired another test was performed at 5.5 MPa (test 16) giving a significantly lower permeability than test 1 and 2 in table 3.7, but more in line with the other results of this sample (fig. 3.5). Probably a small leak was already present during tests 1 and 2, which makes test 16 a more reliable result.

CO<sub>2</sub> permeabilities of sample CM06 decreased with increasing pressure. This trend is not observed in the argon data; argon permeabilities are nearly constant. Also leaving the sample pressurized overnight does not seem to have any effect on the permeability, while CO<sub>2</sub> permeabilities were clearly influenced by this.

Relatively large differences occur between permeability data of sample CM06 and CM12. The measured permeability of sample CM12 is about 4 times higher than the permeability of sample CM06. This might be due to a difference in pore size distribution. When the amount of very small pores, suitable for argon but not for CO<sub>2</sub> transport, is higher in sample CM12 the result can be a higher argon permeability. Also the presence of a leak in sample CM12 cannot be excluded and is possible to explain the higher permeability.

Furthermore, the argon permeability of sample CM12 increases with increasing pressure, while the argon permeability of sample CM06 was nearly constant. A constant permeability was expected for sample CM12 or, if the Klinkenberg effect is present, a decrease in permeability with increasing pressure.

##### Wet experiments

When averaging the permeabilities measured for sample CM06 a clear negative trend can be observed in the data (fig. 3.7). This means permeability decreases with increasing pressure. However, when separating the data of the first and second day of measurement, this negative trend disappears and the permeability turns out to be relatively constant. But permeabilities measured on the first day are significantly higher than those measured on the second day (fig. 3.8). This is probably caused by a

difference in water saturation of the sample. At the start of the second day the sample was wetted again and probably more water was added than on the first measurement day. The same effect is observed in the CO<sub>2</sub> permeability data of this sample, where a higher water saturation on the first day probably caused the difference in permeability.

The permeability of sample CM06 under wet conditions is slightly lower than under dry conditions. Since water seems to have a permeability lowering effect this is an expected result. However, the difference is relatively small. This small difference might be explained by the sample not being fully saturated with water.

As for the dry cement, the argon permeability of sample CM12 under wet conditions is clearly higher than the argon permeability of CM06, probably for the same reason as is given above for dry cement. The argon permeabilities measured for sample CM12 under wet conditions have the same parabolic shaped trend as the CO<sub>2</sub> measurements of this sample under dry conditions. The reason why this same trend is not observed in the wet CO<sub>2</sub> and dry argon data of this sample is not clear.

At the start of the second measurement day sample CM12 was again saturated with water. Previously, a large difference was recognized in the permeability between the first and second measurement day, but in this case permeabilities were about equal. This reason for this is probably an equal water saturation of the sample on both days.

When comparing the wet and dry argon permeability data of sample CM12 a significant difference can be recognized. The permeability of wet cement is clearly lower than the permeability of dry cement, which again indicates the permeability lowering effect of water explained later in this chapter.

### 4.3 Problems with cement samples

Initial permeametry measurements on cement samples yielded very low permeability values, if transport took place at all. In some cases transport was even totally blocked. Multiple hypotheses have been found to explain these low permeabilities. Two of them are based on the presence of water in the samples as being the most important reason for the reduced permeability. The first hypothesis is based on a chemical reaction, water together with CO<sub>2</sub> and calcium (which is present in large amount) can precipitate calcite and block the pores. And the second hypothesis is based on the capillary pressure of water. If the surface tension of water is high enough it prevents gas flowing through the sample and permeability will be reduced. The piece of cement from which cores were drilled and samples were cut, has been kept in water for a reasonable time. For that reason it is likely some water is still present in the sample and that is why all other samples were dried before testing. The samples that were dried before testing (sample CM06 and CM12) showed higher permeabilities corresponding to the expected permeability values for this cement type known from earlier research (Carey et al., 2007; Liteanu, 2009).

Sample CM12 has a much higher permeability to argon than CM06. CM12 has been in the oven for a reasonably longer time than CM06, so possibly more water was removed from CM12. But in that case also a difference in permeability between CM12 and CM06 would be expected for the CO<sub>2</sub> experiments on dry cement. Surprisingly these results are about equal, which makes it questionable if the drying time is the reason for the different argon permeabilities. Sample CM12 can have a higher

permeability to argon than sample CM06 due to a higher connectivity of very small pores in CM12. No other explanation has been found to explain the difference in permeability.

#### 4.4 Three hypotheses to explain low permeabilities

The first five cement samples used for experiments showed much lower permeabilities than expected. A reason for this could be the presence of water in the samples. These first samples were not dried before testing and probably still contain a reasonable amount of water. Two different hypotheses have been developed to explain how water can decrease the permeability of cement. The first one is based on a chemical reaction, the second on the capillary pressure. The third hypothesis suggests the equation of state is not fully accurate and gives low permeability values.

##### 4.4.1 Chemical reaction

One hypothesis for the lower permeabilities of the first samples is a chemical reaction, which takes place during the experiments. The combination of materials like portlandite ( $\text{Ca(OH)}_2$ ) or calcium silicate hydrates (CSH) and dissolved  $\text{CO}_2$  is likely to create a chemical reaction. Dissolution of portlandite and CSH, and precipitation of calcite grains in open spaces in the sample will take place. If this happens pores can be blocked and the permeability of a cement sample can be significantly reduced. It is expected, if this is the only permeability reducing process taking place, no decrease in permeability will occur when using argon as transport fluid since  $\text{CO}_2$  is needed to precipitate calcite.

To test if the formation of calcite is capable to block pores in cement and reduce its permeability, experiments have been done using  $\text{CO}_2$  on wet cement leaving the sample (CM06) under pressure for a longer time. The sample was pressurized at 5.5 MPa. Permeability tests were performed on the sample after 24 and 48 hours with constant pressure on the system. The resulting permeabilities are about the same as those for 5.5 and 7.5 Mpa, which were measured directly after building the sample into the system (tests 11 and 12 in table 3.5).

In 48 hours the permeability has not decreased which implies no additional calcite has been precipitated during these 48 hours. This can be explained by a shortage of water in the sample, as this may restrict calcite-precipitation and hence permeability reduction. This can be due to the wetting method (1), which possibly adds an insufficient amount of water to the sample.

The difference in water uptake between the two different wetting methods was investigated. This was done using sample CM06 after all permeability tests were done. The amount of water in the sample after placing a droplet of water on top of the sample was about 8.413 volume percent, while 25.79 volume percent was measured after evacuating the sample in a glass of water. Another test on a new dried sample was done, also using the evacuation technique, and this sample could store 36.39 volume percent of water. So, a clear difference in water uptake between the two methods can be noticed. The technique used for the permeability experiments seems to add an insufficient amount of water to the sample, which could explain why no further drop in permeability occurs after applying  $\text{CO}_2$  pressure on it for a longer time. When using method 2 the permeability can possibly be reduced much further as calcite can be formed more extensively. However, after the wet experiments with  $\text{CO}_2$  the sample was wetted again for the later aging tests, which yielded similar permeabilities as the earlier tests at 5.5 MPa. Thus more water does not automatically mean more permeability reduction.

Experiments were planned using wetting method 2 on sample CM12, but these experiments could not be performed due to damage to the apparatus.

Another important result is the difference between the amount of water taken up by sample CM06 and a fresh sample, using method 2 for both samples. A difference of about 10 volume percent was measured. An explanation for this result can be that sample CM06 was already used in experiments with CO<sub>2</sub> and water whereas the other sample was not. If the pores of CM06 are partly filled with calcite less water can be stored in this sample.

A second indication for calcite formation was found in later experiments. After all wet experiments with CO<sub>2</sub> were performed the sample (CM06) was dried again and a new experiment using CO<sub>2</sub> at 5.5 MPa was performed (see table 3.1). If no chemical reaction takes place it would be expected that the permeability is the same as for dry experiments with CO<sub>2</sub> performed earlier. However, if some calcite has formed pores are blocked permanently and will stay blocked after drying the sample, permanently reducing the permeability. The result shows the permeability is significantly lower than the first dry experiments on 5.5 MPa and is slightly higher than the result of the wet experiments (table 3.5). This seems to be a strong indication that permeability is permanently decreased due to the presence of water and CO<sub>2</sub>.

More evidence for the precipitation of calcite to be the reason for a lowered permeability is given by the results of experiments on anhydrite. The anhydrite sample itself already had a very low permeability and porosity, only little calcite precipitation would be needed to block transport entirely. The first test already took a long time and during the second test after a few days enough calcite may have precipitated to completely block transport.

#### 4.4.2 Capillary pressure effect

The second hypothesis, to explain the lowered permeability found in the results, is also related to the presence of water in the cement samples. Due to the occurrence of water a certain capillary pressure is present in a cement sample. The capillary pressure possibly significantly reduces transport rates of gases like CO<sub>2</sub> and argon, which gives much lower permeabilities than would be expected. This section discusses if this hypothesis can explain the data from the permeability experiments.

Capillary pressure is the difference in pressure across the interface of two immiscible substances. It is described by the Young-Laplace equation:

$$p_c = \frac{2\gamma \cos \theta}{r}$$

Where  $p_c$  is the capillary pressure,  $\gamma$  the surface tension,  $\theta$  the wetting angle, and  $r$  is the effective radius of the interface. So, the capillary pressure is proportional to the surface tension and inversely proportional to the effective radius of the interface. When the surface tension of water is high, also the capillary pressure of water inside the sample will be high, which means there is a large pressure difference over the water-CO<sub>2</sub> or water-argon interface. When the capillary pressure of water is higher than the pressure of CO<sub>2</sub>/argon, gas flow will most probably be reduced or totally blocked.

Furthermore, the capillary pressure is inversely proportional with the effective radius of the interface. In this case the effective radius of the interface is indicated by the pore size of the sample, and the interface itself is the water-CO<sub>2</sub> or water-argon contact. The smaller the pore sizes the higher the

capillary pressure of water in the cement samples will be. So, due to the capillary pressure of water, samples with small pore sizes will have a low permeability to CO<sub>2</sub> and argon. Because the pore size distribution can be highly variable in this type of cement also the permeability of two different samples, or even the local permeability within a single sample, can be variable. On average the pore sizes are relatively large, but the connection between the pores can be narrow and limit transport when water is present. Pore geometry and pore connectivity are important factors used in several models (Yale, 1984; Jing, 1990; Kovscek et al., 1993; Blunt, 1997a,b; Man & Jing, 1999). Since pore connectivity in this type of cement is probably quite well, as permeabilities of dry cement samples are relatively high and thus require a well connected network, it is not very likely transport becomes entirely blocked by the capillary pressure effect.

However, the permeabilities of samples CM06 and CM12 did significantly decrease without transport becoming totally blocked, making this hypothesis likely to be valid. As can be seen in the results, comparing wet and dry results of CO<sub>2</sub> and argon does not give very consistent results. Sample CM12 shows significantly lower permeabilities for argon experiments using wet cement compared to dry cement, whereas the results of sample CM06 do not show such a difference. This inconsistency in the results of the two samples may be caused by the amount of water present in the samples. This implies that sample CM06 did not contain as much water as CM12 did, and then water saturation has a very large effect on the permeability of cement.

Another interesting observation can be made from the results of the CO<sub>2</sub> tests on wet sample CM06. Experiments on the first day yielded low permeabilities, much lower than for dry cement. The next day CM06 was not saturated with water again and permeabilities were suddenly much higher and comparable to the dry cement experiments, indicating that the sample dried during the night. This observation makes this hypothesis more likely as a chemical effect would permanently reduce the permeability.

#### *4.4.3 Error in equation of state near critical point*

The third hypothesis explaining the lower observed permeabilities of the samples suggests that this may be caused by an inaccuracy in the equation of state near the critical point of CO<sub>2</sub>. However, this hypothesis cannot explain all the lowered permeabilities (under wet conditions) because experiments on samples CM06 and CM12 are also performed at non-critical CO<sub>2</sub> conditions.

The critical point of CO<sub>2</sub> (7.38 MPa at 31.1 °C) is very close to the conditions used in this research. Around the critical point the boundary between the liquid and gaseous phase becomes unclear and the state of CO<sub>2</sub> is not comparable to one of both phases anymore. The used equation of state of CO<sub>2</sub> may not take this into account, and the result can be an inaccurate permeability value.

Results of later experiments on samples CM06 and CM12 were reasonable and comparable with other results on cement samples (Carey et al., 2007; Liteanu, 2009). This strongly indicates that the observed discrepancies are not caused by inaccuracies in the equation of state. Also the earlier samples show that experiments clearly take much more time to equalize the pressure, which would not be the case if the lower permeabilities were the result of an inaccuracy in the equation of state. It is very unlikely this hypothesis can explain the low permeabilities found in this research.

#### 4.5 Klinkenberg effect

In this research two different transport fluids have been used to determine the permeability of cement. When no slip takes place in the pores and the Klinkenberg effect does not take place it is expected that permeabilities to CO<sub>2</sub> and argon are equal. This is because of the fundamental assumption that as long as Darcy flow takes place and the flow rate is proportional to the pressure gradient, permeability is a material property and is not affected by the type of transport fluid. But when the Klinkenberg effect is present permeability is different for different gases because of the varying values for the mean free path (Klinkenberg, 1941). Furthermore Klinkenberg provides that the permeability is inversely proportional to the reciprocal mean pressure. The experimental data given in the results will be interpreted here (fig. 4.1-4.8) to determine if the Klinkenberg effect takes place in the cement samples used for this research.

If the Klinkenberg effect takes place a positive linear graph is expected when plotting the permeability against the reciprocal mean pressure. As can be seen in figures 4.1-4.8, representing the data of samples CM06 and CM12, such a trend has only been found for the CO<sub>2</sub> tests on dry cement and the argon tests of sample CM06. Extrapolating the trend line of fig. 4.1 to infinite pressure gives the true permeability of CM06. However this turns out to give a negative value, which is highly unlikely to be correct. Therefore fig. 4.2 was created which uses the mean permeability of tests at the same absolute pressure. This graph gives a true permeability of  $1.71 \times 10^{-17} \text{ m}^2$ , which is lower than the calculated apparent permeability of the order  $10^{-16} \text{ m}^2$ . This difference between the apparent and true permeability is not very large, possibly indicating the presence of the Klinkenberg effect in this sample.

A way to test the validity of these results is to compare them with the argon tests on dry cement for sample CM06, which should give a true permeability equal to the one found for CO<sub>2</sub>. The slope of the argon data is slightly positive as can be seen in fig. 4.3. Extrapolating this trend line gives a true permeability of  $1.65 \times 10^{-17} \text{ m}^2$ , which is very close to the true permeability of the dry CO<sub>2</sub> data. These corresponding values are a relatively accurate indication of the true permeability of this cement sample.

The true permeability of sample CM06 (dry) to CO<sub>2</sub> is an order of magnitude lower than the apparent permeability measured in the experiments, while the true permeability of this same sample to argon is nearly equal. This implies the Klinkenberg effect influences the permeability of this sample to CO<sub>2</sub>, but not to argon. Argon has a smaller mean free path than CO<sub>2</sub> because its molecules are smaller and therefore can move through smaller pores without experiencing slip along the pore walls. Probably the average pore size of the cement is smaller than the mean free path of CO<sub>2</sub> but larger than the mean free path of argon.

Furthermore, the results of the argon experiments on wet CM06 (fig. 4.5) also show a positive linear trend, even a steeper trend than in fig. 4.3 for dry cement. Though, in this case it is difficult to determine if it is the Klinkenberg effect causing this slope. As discussed earlier water decreases the permeability of cement in several possible ways. The lower permeabilities for higher pressures can in this case also be caused by a higher capillary pressure at higher absolute pressures. Calcite formation does not take place because argon is used. It is actually more probable this positive trend, which is significantly steeper than for dry cement, is caused by the influence of water, since for dry cement permeabilities were nearly constant and hardly any slip occurred. It can be assumed pore sizes have

not been changed between dry and wet experiments, so this probably has not affected the amount of slip in the sample. If water only blocked the larger pores in the sample argon could only be transported through the smallest pores. But since no lower permeability was measured using this sample under dry conditions it is assumed that also the smallest pores of sample CM06 do not encounter the Klinkenberg effect.

Fig. 4.4, which shows the results for CO<sub>2</sub> experiments on wet CM06, does not have a clear trend. This is probably caused by an insufficient amount of water left in the sample during the higher pressure experiments. So these results are not suitable for Klinkenberg effect analysis.

The results of CM12, which are given in fig. 4.6-4.8, do not show positive linear trends. Argon experiments on dry cement even give a negatively linear slope while the results for CO<sub>2</sub> on dry cement and argon on wet cement give a peak permeability at intermediate pressures. This makes it difficult to recognize the possible presence of the Klinkenberg effect in this sample. Because these results are very different from what would be expected, the possible presence of a leak in sample CM12 has to be taken seriously.

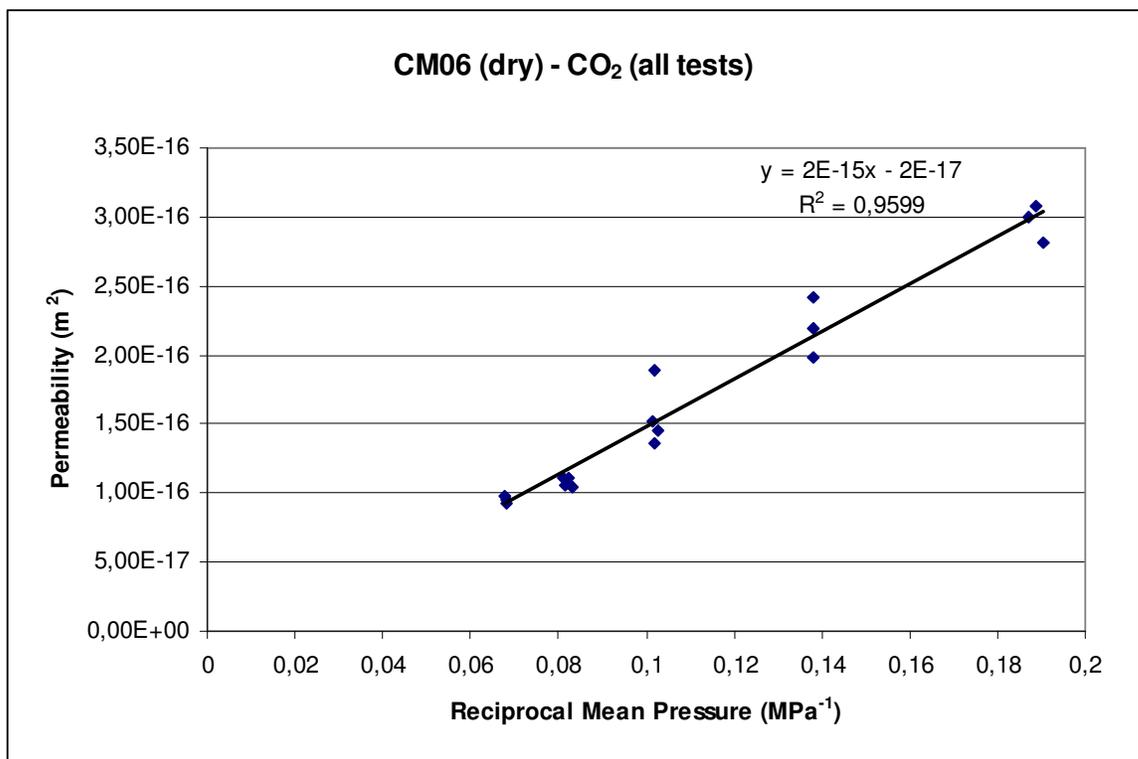


Fig. 4.1: Permeabilities of all tests done for sample CM06 under dry conditions using CO<sub>2</sub> plotted against the reciprocal mean pressure. The trend line through these data shows the permeability at infinite pressure has a negative value, which is highly unlikely. Because of this for the other graphs the mean permeability is used.

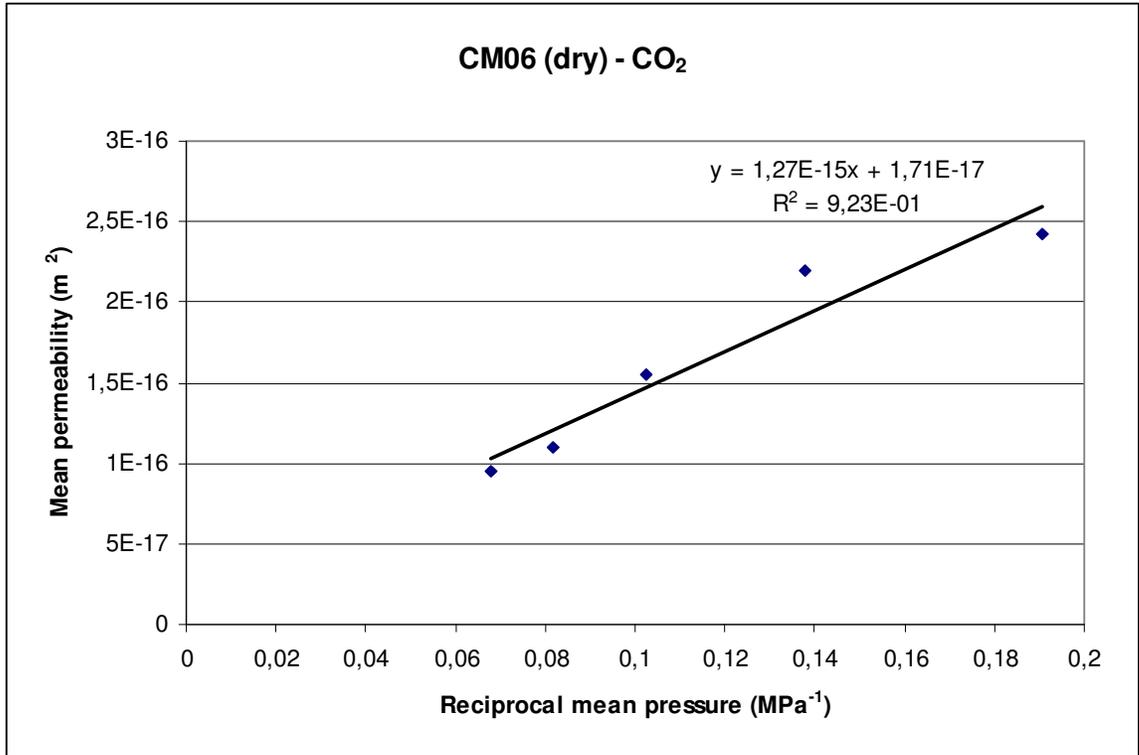


Fig. 4.2: Mean permeabilities of sample CM06 under dry conditions using CO<sub>2</sub> plotted against the reciprocal mean pressure. In this case an expected positive linear trend is the result and furthermore at infinite pressure the permeability has a positive value.

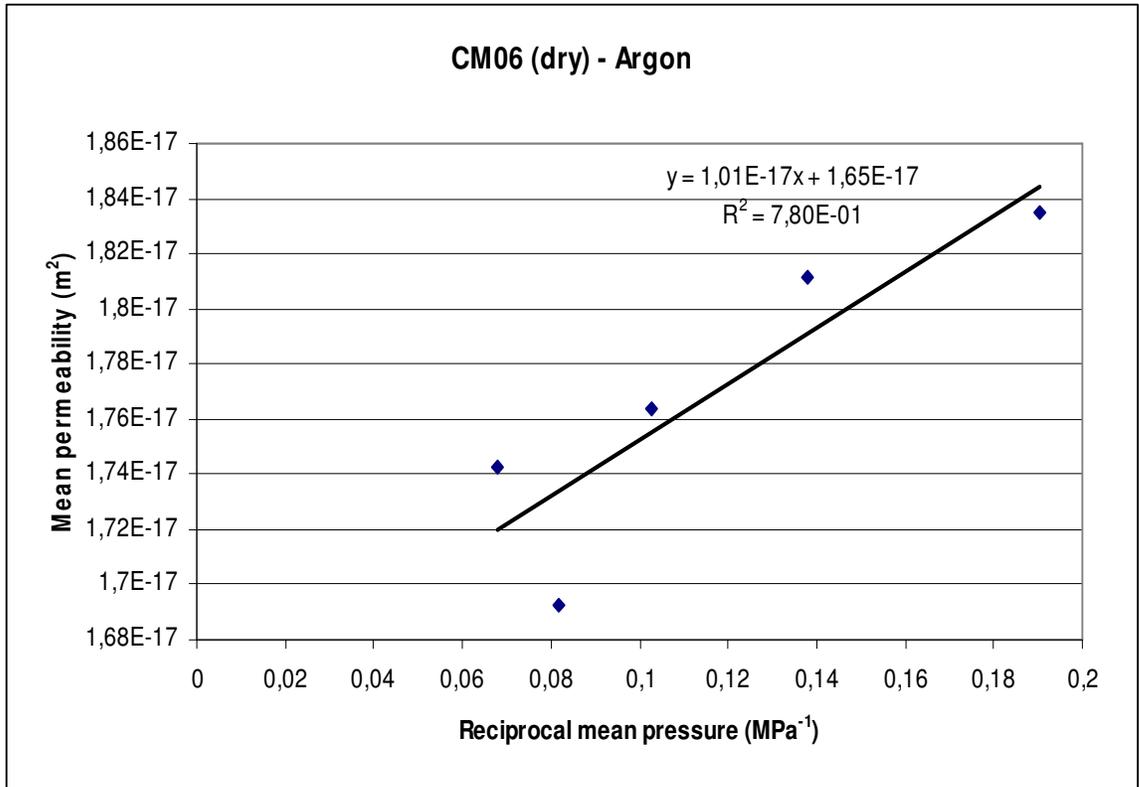


Fig. 4.3: Mean permeabilities plotted against the reciprocal mean pressure for sample CM06 under dry conditions using argon. In this figure some unreliable test results at 5.5 Mpa were left out. The result is a much shallower trend line with a permeability at infinite pressure which is much higher as found in the results of CO<sub>2</sub>.

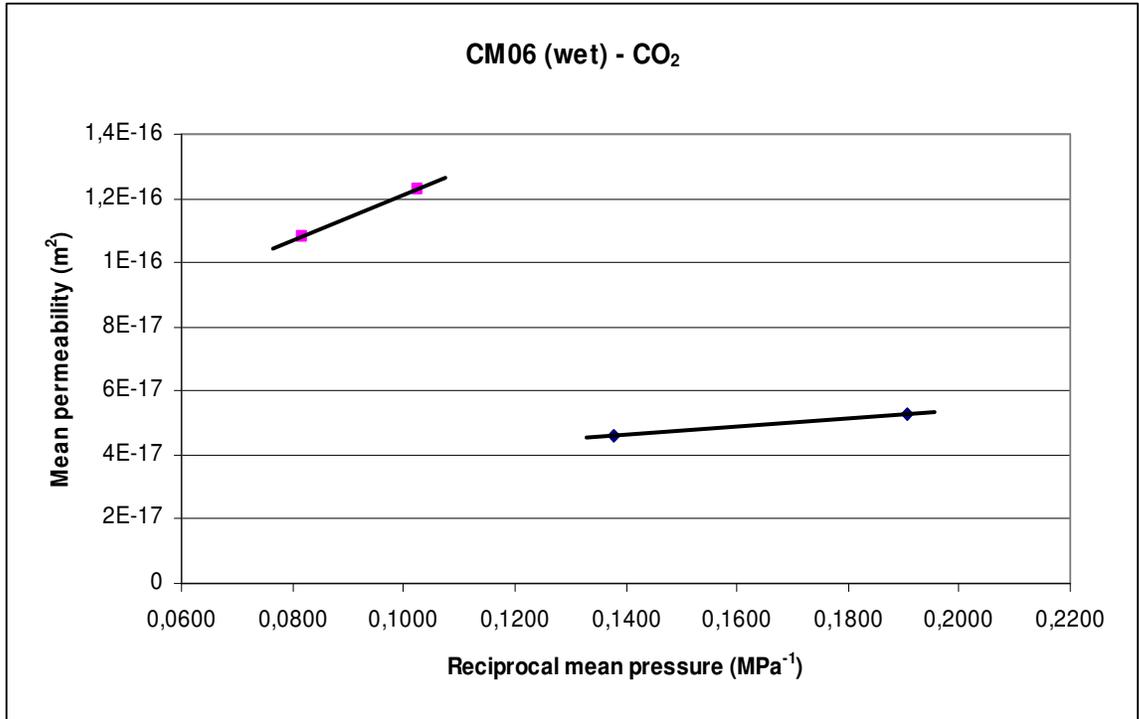


Fig. 4.4: Mean permeability to CO<sub>2</sub> of sample CM06 under wet conditions plotted against the reciprocal mean pressure. No distinguishable trend can be observed in this graph and it is not possible to determine the presence of the Klinkenberg effect.

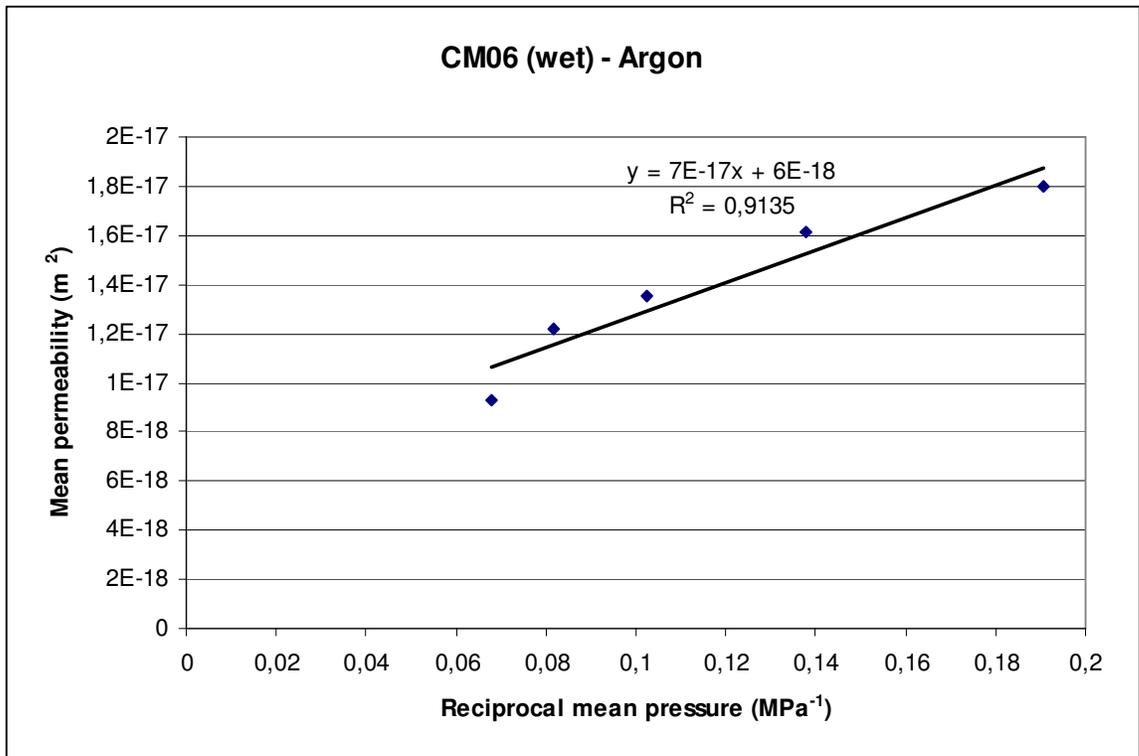


Fig. 4.5: Mean permeability to argon of sample CM06 under wet conditions plotted against the reciprocal mean pressure. Also in this case a positive linear trend line is the result. Remarkable is the permeability at infinite pressure, which is much lower than expected.

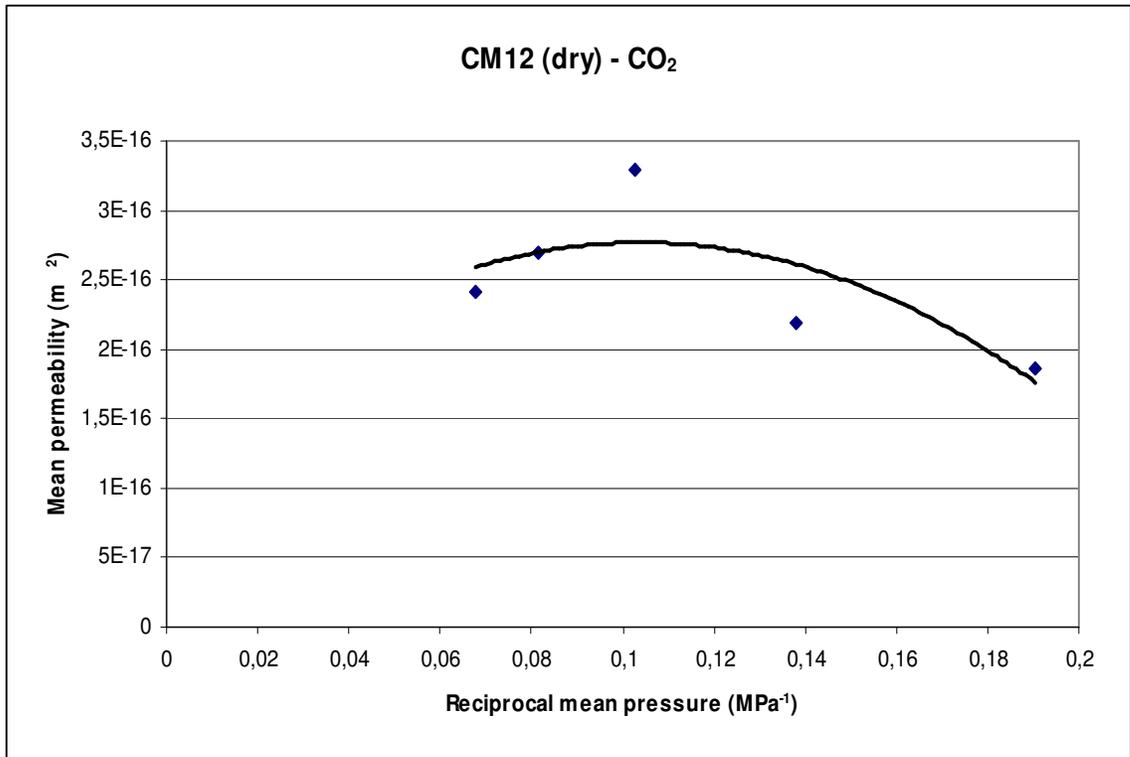


Fig. 4.6: Mean permeability to CO<sub>2</sub> of sample CM12 under dry conditions plotted against the reciprocal mean pressure. This data set has no trend comparable to what would be expected when the Klinkenberg effect is present. No positive linear line can be recognized.

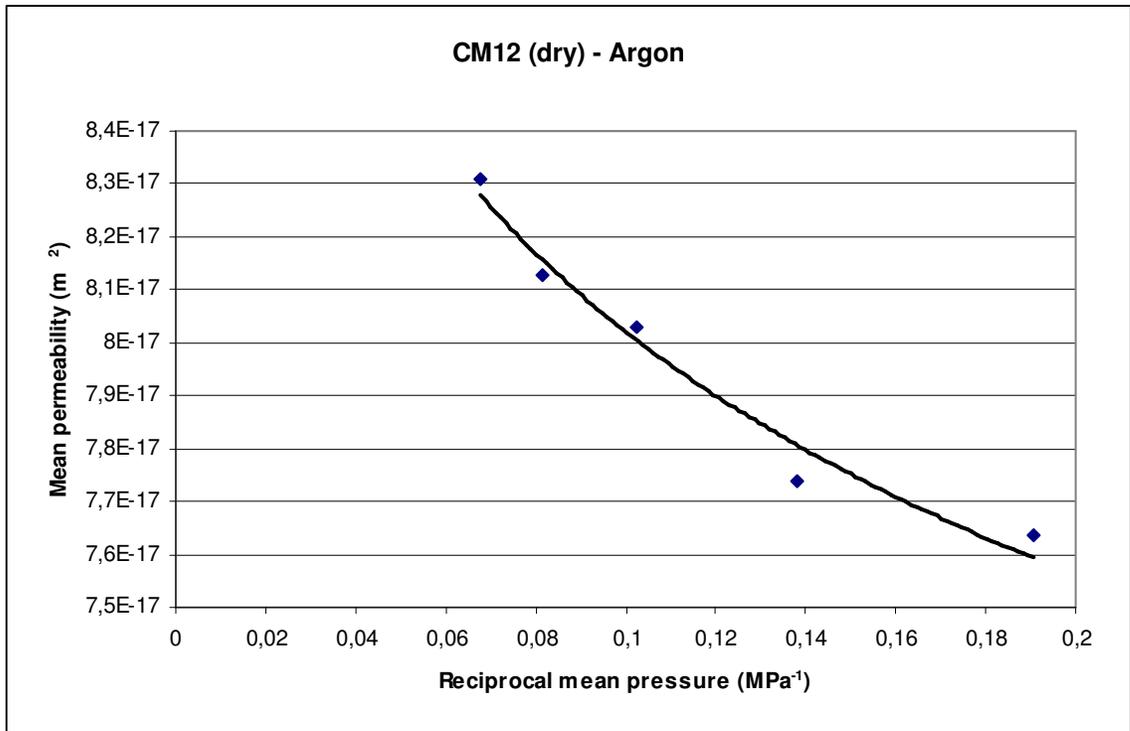


Fig. 4.7: Mean permeability to argon of sample CM12 under dry conditions plotted against the reciprocal mean pressure. In this graph a negative trend in the data can be observed while a positive linear trend is expected.

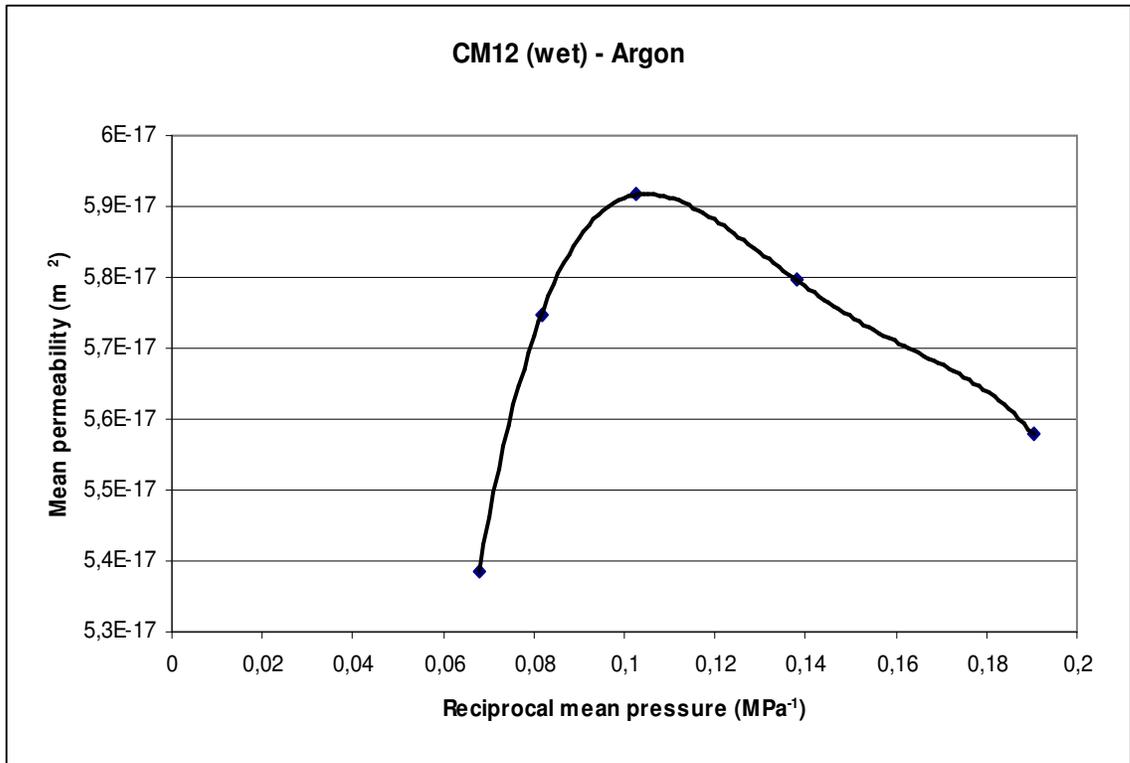


Fig. 4.8: Mean permeability to argon of sample CM12 under wet conditions plotted against the reciprocal mean pressure. Just as for the CO<sub>2</sub> tests on dry sample CM12 the trend becomes negative and has a parabolic shape.

## 5. Conclusions and implications

In this research permeability measurements were performed on two cement samples. The results of the two samples have been compared and discussed and the most important conclusions are summarized below:

- ◆ For both samples CM06 and CM12 permeabilities of wet cement are clearly lower than permeabilities of dry cement. This is a strong indication that water has a permeability lowering effect. Two hypotheses have been developed to explain this effect: the precipitation of calcite, and a capillary pressure effect. A third hypothesis to explain the low permeabilities is based on an inaccuracy in the equation of state near the critical point. The last one turned out to be highly unlikely, while serious indications for precipitation of calcite have been found like lower permeabilities for redried samples. However, leaving a wet sample at CO<sub>2</sub> pressure for a longer time does not lower the permeability, which makes this hypothesis more questionable, although this could also be explained by a shortage of water in the sample. Also the capillary pressure can explain the lowered permeabilities. For example after performing wet experiments, again higher permeabilities were observed. Probably because the water in the sample evaporated. In this case it is no permanent effect, but probably a capillary pressure effect.

The experiments show the first and second hypothesis can both explain the lowered permeabilities. This also makes it highly possible not one of these processes takes place, but both of them at the same time.

- ◆ The Klinkenberg effect has been recognized in the CO<sub>2</sub> tests on dry cement and in argon tests for sample CM06. Positive linear graphs were found in permeability vs. reciprocal mean pressure plots for these tests. The true permeabilities calculated for the tests on dry cement, using both CO<sub>2</sub> and argon, were relatively close to each other which would be expected for different gasses. It turned out that the true permeability of this cement to CO<sub>2</sub> is about a magnitude lower than the apparent permeabilities. The results of the argon tests on wet cement for CM06 were not very reliable and the other tests on sample CM06 and CM12 did not show trends that would be expected when the Klinkenberg effect is present. True permeabilities could only be calculated for CM06, which makes the result relatively inaccurate. As explained earlier it was not possible to create more well working samples.
- ◆ As can be seen in the results the permeability of dry cement samples is relatively high and a significant amount of CO<sub>2</sub> is transported through this material. This would be problematic for the integrity of an old hydrocarbon reservoir used for CO<sub>2</sub> storage, since these reservoirs are often penetrated by a large amount of boreholes and significant amounts of CO<sub>2</sub> can leak to the surface. However, when water is present the permeability decreases significantly and reduces the amount of leakage. It can be concluded that this type of cement can most probably be used without high risks, but only if a sufficient amount of water is present. For dry areas with hardly any ground water it is recommended to use other methods to seal the CO<sub>2</sub> reservoirs.

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